MECHANISTIC STUDIES OF Ru (III) AND Ir (III) CATALYSED OXIDATION OF BIOLOGICALLY ACTIVE COMPOUNDS BY Cu (II) COMPLEXES

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CERTIFICATE

This is to certify that the thesis entitled "Mechanistic studies of Ru(III) and Ir(III) catalysed oxidation of Biologically active compounds by Cu(II) complexes" submitted for the degree of Doctor of Philosophy of the Bundelkhand University, Jhansi (U.P.) is a record of bonafide research work carried out by Sri Alok Awasthi under my guidance and supervision.

The work embodied in this thesis or a part thereof, has not been submitted for the award of any other degree or diploma. All the help and assistance received during the course of present investigations have been duly acknowledged.

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CHAPTER I

INTRODUCTION

INTRODUCTION

Catalytic processes involving oxidation of organic compounds are useful and have always been in greater demand. Several of such processes were mastered by the common man merely using their powers of observations and analysis. In general the catalytic reactions might be divided into two main groups. The first group is concerned with heterogeneous reactions in which the reactants and catalyst have their different phases. The second group is concerned with homogeneous reactions in which the reactants and catalyst are found in the same phase. Of course, the first group of catalysed reactions have considerable applications in modern chemical industries and have, therefore, been widely subjected to studies and investigations. A survey of literature shows that the studies in the oxidation of organic compounds involving an effective heterogeneous catalyst are also much substantial as compared to homogeneous one. Almost very little incentives appear to have been given to work out the kinetics and mechanism of even well known homogeneously catalysed processes. Apparently, homogeneously catalysed processes have little scope of their being useful in synthetic work, yet these are of equal applicability and involve considerable academic interest from mechanistic point of view.

The homogeneously catalysed biological reactions are still a mysty and put a challenge to the scientists devoted

in this field. The enzyme catalysed reactions are a good bet. Inspite of the general incentive required in investigating mechanistic details of these processes, the subject matter of the oxidation of organic compounds using either type of the catalyst is far scanty in solution kinetics.

Copper(II) - Copper(I) couple was used for the oxidation of ethylen to acetaldehyde in the presence of palladium chloride used as a homogeneous catalyst[1]. Direct addition of hydrogen peroxide to olefinic compounds to produce glycols catalysed by various inorganic salts has been described very well by Mugdan and Young[2]. These reactions were used for the synthetic work with no adequate attempt made to the kinetics and mechanism of the reactions which occur in a recent studies. A successful kinetic study was made by Martell and Khan in the metal ion and metal chlorate catalysed oxidation of ascorbic acid by molecular oxygen[3].

The oxidation of organic compounds by Ce(IV) catalysed by chromium(III) salts is an example of homogeneous catalysis. The proposed mechanism shows a rapid reaction between chromium(III) and Cerium(IV) followed by a rate determining reaction betwéen the organic substrate and the chromium which is in a valence state greater than three (most likely it is chromium (IV)). This system exemplifies the fact that

oxidation potentials can not be used as a reliable guide to rate of oxidation, since Ce(IV) has a higher oxidation potential than chromium(VI). Several reactions of industrial use are catalysed by vanadium in homogeneous reaction.

Osmium tetroxide has been described a very interesting and effective catalyst for the oxidation of organic compounds in solution. The catalytic actions of the reagent are well known with several couples.

The most thoroughly investigated type of reactions in solution are the electron - transfer reactions between an oxidant and a reductant. The study of such reactions, also known as redox reactions, is of great interest because of its vast application in understanding the nature of chemical process involved. An oxidation or reduction will be any reaction that converts one compound to different oxidation state. The most of atoms and free radicals having deficient electron shell are capable of acting as oxidising agents by abstracting electrons from other species and thus becoming ions themselves. The oxidising or reducing capacity of a compound is often determined by its redox potential. The common oxidising agent are higher valent compounds such as heptavalent manganese in the form of permanganate, hexavalent chromium in the form of chromic acid, cerium(IV) sulphate, hexacyanoferrate (III), potassiumiodate, peroxydisulphate and chloramine-T etc.

There are several factors which determine the mechanism of redox reactions in solution such as the order of reaction with respect to both oxidant and reducing substrate, the effect of solvent and dielectric constant, effect of ionic strength, effect of pH etc. The thermodynamic parameters viz. energy of activation, free energy of activation, entropy of activation also give some informations about mechanism. In catalysed reactions several short-lived intermediates may be formed with the catalyst and thus the mechanism of a catalysed reaction may be quite different to that of the uncatalysed one, although the end products in both cases may be the same. There may be a number of intermediate products which are extremely reactive and hence short-lived. The identification of these intermediate products and the reaction products is another important factor which leads to the elucidation of reaction mechanism.

Several oxidising and reducing agents have been used for overall as well as step by step oxidation and reduction purposes. Kinetics and mechanism of several redox reactions involving potassiumpermanganate, peroxydisulphate, hydrogen peroxide, hexacyanoferrate(III), Cerium(IV), platinum(IV), chromium (VI), arsenic (III), cobalt (III), selenium(IV), copper(II), chloramine-T, bromamine-T, N-chlorosuccinimide, N-bromosuccinimide, N-bromoacetamide etc. have been studied.

The role of several catalysts viz. vanadium(V), osmium(VIII), Cd(II), Co(III), Mo(VI), Ru(III), Pd(II) etc. during such redox reactions has been studied extensively.

The kinetics of ruthenium(III) catalysed oxidation of aldoses[4] by N-bromosuccinimide in presence of mercuric acetate, sulphuric acid and 10% (V/V) acetic acid have been studied. The reactions were first-order in N-bromosuccinimide in presence and absence of the catalyst. The order in substrate was unity in absence of the catalyst and changes to fractional order in the presence of the catalyst. Increase in H^+ retarded the reaction rate. The order of reactivity of different aldoses was observed, to be D - arbinose > D - xylose > D - galactose > D - mannose > D - glucose. The mechanism involving the α - anomer of aldose as the reactive species of the substrate has been proposed.

The kinetic studies on the ruthenium(III) catalysed oxidation of amino acids[5] viz. glycine, α - alanine, β - alanine, leucine, phenylglycine by N-bromosuccinimide in the presence of mercuric acetate have been investigated. The oxidation products were identified as corresponding aldehyde, ammonia and CO_2. The order of the reaction in N-bromosuccinimide was always unity. In presence of catalyst the order of reaction in substrate was fractional. The studies on ruthenium(III) catalysed oxidation of acetophenones by

N-bromosuccinimide in the presence of mercuric acetate have also shown a similar kinetics. The order of reactivity observed among different acetophenones was p - NO_2 > m - NO_2 > p - Cl > m - OCH_3 > -H > m-CH_3 > P - CH_3 > p - OCH_3 acetophenone.

The kinetics of ruthenium(III) catalysed oxidation of chloroacetic acids[7] by N-bromosuccinimide(NBS) have also been investigated in the presence of sulphuric acid and mercuric acetate. The order of the reaction in NBS was unity in the presence as well as in absence of the catalyst. However, the order in [substrate] in the absence of Ru(III) was unity, which changed to fractional in the presence of ruthenium(III). Increase in $[H^+]$ retarded the reaction rate. The kinetics of ruthenium(III) catalysed oxidation of benzaldehyde and substituted benzaldehyde by NBS in the presence of mercuric acetate have been investigated[8]. The reaction showed a first-order in [NBS] and a fractional order in [substrate] as well in the [catalyst] . A mechanism involving NBS - substrate complex has been proposed ruthenium(III) catalysed oxidation of unsaturated acids viz. maleic acid and fumaric acid[9] by NBS has also shown a similar kinetics.

Earlier, the kinetics of oxidation of propionic acid and isobutyric acid by N-bromoacetamide in the presence of

mercuric acetate as scavenger for bromide ion[10] in the presence of acid solution of iridium(III) chloride[11] as homogeneous catalyst have been studied. The first order kinetics in N-bromoacetamide at its low concentration has been reported to shift to zero - order at higher concentrations. First order dependence on iridium(III) chloride was reported and zero - order in reducing acids was shown. Iridium(III) chloride in acidic medium was shown to participate in reaction as catalyst with its $[IrCl_5H_2O]^{2-}$ species as catalytic species.

Iridium(III) chloride catalysed oxidation of valeric acid[12] by N-bromoacetamide also showed first-order dependence on iridium(III) chloride. The kinetics and mechanism of iridium(III) chloride catalysis in N-bromoacetamide oxidation of some acids viz. lactic acid and glycollic acid in perchloric acid media have been recently reported[13]. First order kinetics in N-bromoacetamide, iridium(III)chloride and Hg(II) was observed while inverse first order in H^+ and acetamide was observed. Decreasing effect of added chloride ions was observed. $(IrCl_5 \cdot H_2O)^{2-}$ was taken as catalytic species of iridium(III) chloride. Mercuric acetate used as Br^- scavenger was found to have catalytic effect. Thus Ir(III) and Hg(II) co - catalyst mechanism was proposed.

Earlier Singh et al[14] studied oxidation kinetics of some reducing sugars by alkaline Cu(II) and observed that the

rate of oxidation is independent of Cu(II) concentration and is first-order both with respect to hydroxide ion and reducing sugars concentrations. They further reported that the reaction has an induction period and shows autocatalysis due to Cu_2O produced in the system. These results were confirmed by Marshall and waters[15] from the oxidation kinetics of D-glucode, benzoin and acetoin by alkaline Cu(II) using various complexing agents and also by Singh et al[16]. from the oxidation kinetics of some reducing sugars by alkaline Cu(II) without using any complexing agent. Wiberg and Nigh[17] have studied the oxidation of α - hydroxyacetophenone by Cu(II) in aqueous pyridine and they have supported the explanation of Singh[14,16] et al lower concentrations of Cu(II). The essential kinetic features of oxidation of keto sugars by ammoniacal Cu(II) have been studied for the first time. The system becomes homogeneous due to formation of soluble Cu(I) - ammonia complex[18] i.e. $[Cu(NH_3)_2]^+$. In order to find out whether Cu(II) plays the similar role in the presence of ammonia as observed in the role of Ag(I)[19] in the presence of ammonia or as observed in the role of Cu(II) in presence of complexing agents such as tartarate, citrate, picolinate and pyridine, Singh et. al[20] have studied the kinetics of Cu(II) oxidation of keto sugars viz. D-fructose and L-sorbose by Cu(II) in the presence of ammonia as complexing agent.

Singh et al[21] have also reported the kinetics of oxidation of D-glucode and D-galactose by Cu(II) in the presence of ammonium hydroxide. Kinetics data demonstrated zero - order kinetics in Cu(II) and first-order dependence on $[OH^-]$ & sugar . A general mechanism involving the intermediate enediol anion was proposed. Rate of enolisation as the rate of oxidation of these sugars was evidenced here.

Singh, Sisodia, Parmar, Saxena and Bajpai[22] have studied the kinetics and mechanism of oxidation of D-fructose by $[Cu(C_5H_5N)_4]^{+2}$ in the presence of free pyridine spectrophotometrically. Singh, Parmar, Tiwari, Singh and Gupta[23] have recently reported the oxidation kinetics involving lactose and maltose as reducing sugars and Cu(II) as oxidant in the presence of bipyridyl as complexing agent in alkaline media.

PRESENT WORK

The present investigation includes the study of oxidation of some amino acids viz. glycine and alanine by copper sulphate in the presence of alkaline solution of 2,2 - bipyridyl as complexing agent. The alkaline solution of Na_2CO_3 and $NaHCO_3$ has been used. In addition to above, another redox system containing D-glucose and D-galactose as reducing sugars and $[\text{Copper (bipyridyl)}_2^{2+}]$ as oxidising reagent in the presence of alkali copper sulphate alongwith free bipyridyl forms a complex $[Cu(bip.)_2]^{2+}$ in a soluble state. When the proposed redox system is studied in alkaline medium, $[Cu(bip.)_2^{2+}]$ is reduced to $[Cu(bip.)]^{+}$ which is also soluble. Thus the complexing agent 2,2' - bipyridyl helps in maintaining homogeneous redox system throughout the investigation. The kinetic parameters collected in the present investigation has helped in proposing the reaction path which could give the rate law as

$$\frac{-d\,[Cu(II)]^{*}}{dt} = \frac{k\,[\text{Catalyst}]\,[S]\,[OH^{-}]}{K_2' + [Cl^{-}]}$$

where $[Cu(II)]^{*} = [Cu(bip.)_2^{2+}]$

$[\text{Catalyst}]$ = Either $[Ru(III)]_T$ or $[Ir(III)]_T$

S = Amino Acid or Sugar

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CHAPTER II

EXPERIMENTAL

EXPERIMENTAL

2.1 : MATERIALS EMPLOYED

The samples of D-glucose and D-galactose used were of E.Merck grade . The samples of glycine and alanine were also of E.Merck grade. The solutions of these reducing materials were prepared by dissolving the weighed quantity of these samples in doubly distilled water.

The other chemicals used were cupric sulphate, 2,2' - bipyridyl in 25% ethyl alcohol, potassium chloride, all of A R (B D H) quality.

The standard solution of cupric sulphate was prepared by dissolving an exact amount of (BDH) AR grade sample in double distilled water.

The solutions of sodium carbonate and sodium bicarbonate were also prepared by dissolving their weighed samples in doubly distilled water and standardised with the help of standard solution of hydrochloric acid.

Standard solution of potassium chloride was also prepared by dissolving an exact amount of KCl (AR, BDH).

Solutions of ruthenium trichloride and iridium trichloride were also prepared by dissolving their 1 gm samples (Johnson & Matthey) in 100 ml HCl solution (0.1N) and then making up these solutions to 500 ml.

Solution of potassium dichrome was prepared by exact weighing of its sample in dissolving the weighed amount in desired volume of water.

2.2 : PROCEDURE

The kinetic studies involving glycine alanine, D-glucose and D-galactose as reducing materials and copper (II) as oxidant have been made in alkaline media in the presence of 2,2' bipyridyl as complexing agent. The system remains homogeneous due to soluble $[Cu(Bip.)_2]^{2+}$ and $[Cu(Bip)_2]^{+}$ complexes throughout the course of reaction.

The reaction mixture was prepared by mixing the requisite volume of Cu(II), 2,2' - bipyridyl and alkali solutions (Na_2CO_3 and $NaHCO_3$), ruthenium(III) chloride (in case of glycine and alanine) and iridium(III) chloride (in case of D-glucose and D-galactose) and potassium chloride solution. The reaction mixture was taken in a reaction bottle which was placed in an electrically e operated thermostat($\pm$ 0.10). In another bottle requisite volume of sugars or amino acid solution was also placed in the same thermostate to attain the termal equilibrium. When both the bottles had attained the desired temperature, then the requisite volume of sugar or amino acid was mixed with the reaction mixture of another bottle vigorously to initiate the reaction. Immediately time was noted for

zero time. An aliquot (5 ml) of this reaction mixture was immediately taken out and titrated against standard solution of potassium dichromate. At different time intervals Cu(I) produced in the reaction mixture (5 ml) was titrated and readings were recorded. These recorded values helped in calculating ko values from which ks (standard zero-order rate constant) values were calculated by the formula

$$ks = \frac{ko \times s}{V}$$

where s is strength of titrant (i.e. $K_2Cr_2O_7$) and V is 5 ml.

The order of the reactions with respect to Cu(II) is determined by keeping reducing sugars or amino acids concentration in large excess as compared to that of Cu(II). Under such condition the velocity of the reaction will mainly be determined by the change in the concentration of Cu(II) ion. It has been observed that in each experiment there has not been much change in k_o i.e. ($\Delta x/\Delta t$) values. Thus in each kinetic runs zero-order kinetics in Cu(II) ion is followed.

The order of the reaction with respect to any other reactive species has been determined by the formula

$$k_1 = \frac{k_s}{[\text{reactive species}]}$$

This shows that if k_s remain constant at different [reactive species], the order in reactive species in zero. Similarly, if k_1 are constant at different concentrations of reactive species, the reaction is first-order in reactive species.

CHAPTER III

DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO COPPER SULPHATE IN Ru(III) CATALYSED OXIDATION OF AMINO ACIDS AND Ir(III) CATALYSED OXIDATION OF SUGARS

3 : DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO COPPER SULPHATE IN Ru(III) CATALYSED OXIDATION OF AMINO ACIDS AND Ir(III) CATALYSED OXIDATION OF SUGARS

In this chapter an attempt has been made to study the dependence of the reaction between Cu(II) and amino acids on copper sulphate and determination of order of the reaction between Cu(II) and sugars with respect to copper sulphate. Copper sulphate - amino acids system has been studied in alkaline solution of ruthenium(III) chloride in the presence of 2,2' - bipyridyl as complexing reagent while copper sulphate - sugars redox system has been investigated in the presence of alkaline solution of iridium(III) chloride using again 2-2' - bipyridyl as complexing reagent. Alkaline nature of the reaction mixture has been maintained with solutions of Na_2CO_3 and $NaHCO_3$. The results of various experiments performed at different concentrations of copper sulphate but at fixed concentrations of all other reactants have been given in tables 3.1 - 3.6, tables 3.7 - 3.12, tables 3.13 - 3.18 and tables 3.19 - 3.24 for the oxidation of glycine, alanine, D-glucose and D-galactose respectively under the isolation conditions of experiments. It has been observed that both the redox systems follow similar kinetics with

respect to copper sulphate. Zero order rate constant i.e. k_s has been calculated by the formula $k_s = \frac{ko \times s}{V}$

where ko is $\Delta x/\Delta t$ given in 3rd column of each table, S is the strength of potassium dichromate used as titrant to estimate Cu(I) produced at different time intervals and V is volume (5 ml here in present case) of the reaction mixture taken out at different time intervals for estimation. In each table 2 - 2' bipyridyl has been written as free bip for the sake of simplicity and convenience. Similarly Ru(III) or Ir(III) have been written for Ru(III) chloride and Ir(III) chloride respectively.

TABLE 3.1

$[CuSO_4]$ = 1.00×10^{-3}M, [Glycine] = 10.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

$[Na_2CO_3]$ = 5.00×10^{-2}M, $[NaHCO_3]$ = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8, Temp. 30°C

μ = 17.50×10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (M/2000) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml / min
0	0.00	--
10	0.62	6.20
20	1.26	6.40
30	1.87	6.10
40	2.47	6.00
50	3.10	6.30
60	3.72	6.20
70	4.30	5.80
80	4.90	6.00
90	5.49	5.90
100	6.14	6.50

Average k_O = 6.14×10^{-2} ml min^{-1}

k_s (zero-order rate constant) = 6.14 $\times 10^{6}$ mol l^{-1} min^{-1}

where $k_s = k_O \times s/v$, s is strength of the titrant i.e. $K_2Cr_2O_7$ solution and v is the volume of reaction mixture estimated with $K_2Cr_2O_7$ solution used here as titrant

TABLE 3.2

$[CuSO_4]$ 1.25x10^{-3}M, [Glycine] = 10.00x10^{-2}M,

[Free Bip.] = 5.00x10^{-3}M, [Ru(III)] = 4.00x10^{-6}M

$[Na_2CO_3]$ = 5.00x10^{-2}M, $[NaHCO_3]$ = 2.00x10^{-3}M,

[KCl] = 1.00x10^{-3}M, pH = 10.8 and Temp. 30^{o}C

μ = 17.50 x 10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (N/2000) in ml	10^2 ko = $\frac{\Delta x}{\Delta t}$ ml / min
0	0.66	- -
10	0.66	6.60
20	1.28	6.20
30	1.88	6.00
40	2.52	6.40
50	3.10	5.80
60	3.70	6.00
80	4.96	6.30
100	6.20	6.20
120	7.40	6.00
140	8.68	6.40

Average ko = 6.19 x 10^{2} ml min^{-1}

k_s = 6.19 x10^{-6} mol l^{-1} min^{-1}

TABLE 3.3

$[CuSO_4] = 2.00 \times 10^{-3}$ M, [Glycine] $= 10.00 \times 10^{-2}$ M

[Free Bip.] $= 5.00 \times 10^{-3}$ M, [Ru(III)] $= 4.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

[KCl] $= 1.00 \times 10^{-3}$ M, pH = 10.8 Temp. 30°C

$\mu = 17.50 \times 10^{-2}$ M

Time (min.)	Volume of $K_2Cr_2O_7$ (N/2000) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
10	0.58	5.80
20	1.18	6.00
30	1.76	5.80
40	2.38	6.20
50	3.02	6.40
60	3.64	6.20
80	4.84	6.00
100	6.12	6.40
130	8.10	6.60
160	10.02	6.40

Average $k_0 = 6.18 \times 10^{-2}$ ml min^{-1}

$k_s = 6.18 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.4

$[CuSO_4] = 3.00 \times 10^{-3}$M, $[\text{Glycine}] = 10.00 \times 10^{-2}$M

$[\text{Free Bip.}] = 5.00 \times 10^{-3}$M, $[\text{Ru(III)}] = 4.00 \times 10^{-6}$M

$[Na_2CO_3] = 5.00 \times 10^{-2}$M, $[NaHCO_3] = 2.00 \times 10^{-3}$M

$[KCl] = 1.00 \times 10^{-3}$M, pH = 10.00 and Temp. 30°C

$\mu = 17.50 \times 10^{-2}$M

Time (min.)	Volume of $K_2 Cr_2 O_7$ (N/650) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.08	21.16*
10	1.18	2.00
20	1.40	2.20
30	1.62	2.20
40	1.86	2.40
60	2.32	2.30
100	3.22	2.25
140	4.08	2.15
180	4.98	2.25
220	5.82	2.10
260	6.62	2.00

Average $k_o = 2.18 \times 10^{-2}$ ml min^{-1}

$$k_s = 2.18 \times 10^{-2} \times \frac{N}{650 \times 5} = 6.71 \times 10^{-6} \text{ mol l min}^{-1}$$

* This value is neglected

TABLE 3.5

$[CuSO_4] = 4.00\times10^{-3}M$, $[Glycine] = 10.00\times10^{-2}M$

$[Free\ Bip.]\ 5.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.8 and Temp. 30°C

$\mu = 17.50\times10^{-2}M$

Time (min.)	Volume of $K_2Cr_2O_7$ (N/5000) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.68	33.60*
15	1.84	1.60
25	2.00	1.60
45	2.30	1.50
75	2.76	1.53
100	3.16	1.60
130	3.64	1.60
160	4.10	1.53
200	4.76	1.65
240	5.36	1.50

Average k_o (excluding *) $= 1.56 \times 10^{-2}$ ml min^{-1}

$k_s = 6.24 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.6

$[CuSO_4]$ = 5.00×10^{-3}M, [Glycine] = 10.00×10^{-2}M

[Free Bip.] 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

$[Na_2CO_3]$ = 5.00×10^{-2}M, $[NaHCO_3]$ = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and Temp. 30°C

μ = 17.50×10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (N/500) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml / min
0	0.00	--
10	1.80	18.00*
20	1.96	1.60
30	2.12	1.60
50	2.42	1.50
80	2.88	1.53
120	3.52	1.60
160	4.12	1.50
200	4.74	1.55
240	5.38	1.60
280	5.98	1.50

Average ko 9 excluding *) = 1.54×10^{-2} ml min^{-1}

k_s = 6.16×10^{-6} mol l^{-1} min^{-1}

TABLE 3.7

$[CuSO_4] = 1.00\times10^{-3}M$, $[\text{Alanine}] = 10.00\times10^{-2}M$

$[\text{Free Bip.}] = 5.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.8 and Temp. 30°C

$\mu = 17.50 \times 10^{-2}M$

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml / min
0	0.00	--
10	0.42	4.20
20	0.86	4.40
30	1.26	4.00
45	1.90	4.26
60	2.56	4.40
80	3.40	4.20
100	4.22	4.10
120	5.02	4.00
140	5.86	4.20
160	6.68	4.10

Average $k_0 = 4.18 \times 10^{-2}$ ml min^{-1}

$k_s = 4.18 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.8

[$CuSO_4$] = 1.25×10^{-3}M, [Alanine] = 10.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and Temp. 30°C

μ = 17.50×10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}M) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
10	0.40	4.00
20	0.82	4.20
30	1.26	4.40
40	1.68	4.20
60	2.50	4.10
80	3.34	4.20
100	4.14	4.00
120	4.98	4.20
140	5.84	4.30
160	6.66	4.10

Average k_0 = 4.17×10^{-2} ml min^{-1}

k_s = 4.17×10^{-6} mol l^{-1} min^{-1}

TABLE 3.9

$[CuSO_4] = 2.00 \times 10^{-3}$ M, [Alanine] $= 10.00 \times 10^{-2}$ M

[Free Bip.] $= 5.00 \times 10^{-3}$ M, [Ru(III)] $= 4.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

[KCl] $= 1.00 \times 10^{-3}$ M, pH = 10.8 and Temp. 30°C

$\mu = 17.50 \times 10^{-2}$ M

Time (min.)	Volume of $K_2Cr_2O_7$ (0.5×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
10	0.44	4.40
20	0.86	4.20
40	1.66	4.00
60	2.48	4.10
80	3.32	4.20
100	4.12	4.00
125	5.12	4.00
150	6.22	4.40
175	7.28	4.24
200	8.38	4.40

Average $k_o = 4.19 \times 10^{-2}$ ml min^{-1}

$k_s = 4.19 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.10

[$CuSO_4$] = 3.00×10^{-3}M, [Alanine] = 10.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and Temp. 30°C

μ = 17.50×10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (1.54×10^{-3}M) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
10	1.34	13.40*
20	1.46	1.40
40	1.72	1.30
70	2.16	1.46
100	2.58	1.40
140	3.12	1.35
180	3.68	1.40
220	4.22	1.35
260	4.74	1.30
300	5.28	1.35

Average k_o (excluding *) = 1.37×10^{-2} ml min^{-1}

$$k_s = \frac{1.37\times10^{-2} \times 1.54\times10^{-3}}{5} = 4.22 \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1}$$

TABLE 3.11

[$CuSO_4$] = 4.00×10^{-3}M, [Alanine] = 10.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and Temp. 30°C

μ = 17.50×10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (2.00×10^{-3}M) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$
0	0.00	- -
10	1.48	14.80*
25	1.64	1.06
50	1.88	0.96
75	2.14	1.04
100	2.40	1.04
140	2.80	1.00
180	3.22	1.05
220	3.66	1.10
260	4.08	1.05
300	4.50	1.05
350	5.04	1.08

Average k_o (excluding *) = 1.04×10^{-2} ml min^{-1}

$k_s = 4.16 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.12

$[CuSO_4] = 5.00\times10^{-3}$M, $[\text{Alanine}] = 10.00\times10^{-2}$M

$[\text{Free Bip.}] = 5.00\times10^{-3}$M, $[\text{Ru(III)}] = 4.00\times10^{-6}$M

$[Na_2CO_3] = 5.00\times10^{-2}$M, $[NaHCO_3] = 2.00\times10^{-3}$M

$[KCl] = 1.00\times10^{-3}$M, pH = 10.8 and Temp. 30°C

$\mu = 17.50 \times 10^{-2}$M

Time (min.)	Volume of $K_2Cr_2O_7$ (2.00×10^{-3}N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
10	1.50	15.00*
25	1.66	1.06
50	1.92	1.04
75	2.16	0.96
100	2.40	0.96
150	2.90	1.00
200	3.42	1.04
250	3.96	1.08
300	4.48	1.04
350	5.00	1.04

Average k_0 (excluding *) = 1.03×10^{-2} ml min^{-1}

$k_s = 4.12 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.13

$[CuSO_4] = 1.00 \times 10^{-3} N$, $[\text{D-glucose}] = 5.00 \times 10^{-2} M$

$[\text{Free Bip.}] = 5.00 \times 10^{-3} M$, $[Ir(III)] = 5.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 2.00 \times 10^{-3} M$

$[KCl] = 2.00 \times 10^{-3} M$, pH = 10.8 and Temp. 30°C

$\mu = 17.50 \times 10^{-2} M$

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
10	1.50	10.00
15	2.02	10.40
20	2.50	9.60
30	3.50	10.00
40	4.48	9.80
50	5.50	10.20
60	6.50	10.00
70	7.48	9.80
80	8.50	10.20

Average k_0 (excluding *) = 10.00×10^{-2} ml min^{-1}

$k_s = 10.00 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.14

$[CuSO_4] = 1.25 \times 10^{-3}M$, $[\text{D-glucose}] = 5.00 \times 10^{-2}M$

$[\text{Free Bip.}] = 5.00 \times 10^{-3}M$, $[Ir(III)] = 5.00 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 2.00 \times 10^{-3}M$

$[KCl] = 2.00 \times 10^{-3}M$, pH $= 10.8$ and Temp. $30°C$

$\mu = 17.50 \times 10^{-2}M$

Time (mins.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
10	1.50	9.60
15	2.00	10.00
20	2.52	10.40
30	3.52	10.00
40	4.50	9.80
50	5.52	10.20
60	6.52	10.00
70	7.52	10.00
80	8.52	10.00

Average k_0 (excluding *) $= 10.00 \times 10^{-2}$ ml min^{-1}

$k_s = 10.00 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.15

[$CuSO_4$] = 2.00x10^{-3}M, [D-glucose] = 5.00x10^{-2}M

[Free Bio.] = 5.00x10^{-3}M, [Ir(III)] = 5.00x10^{-6}M

[Na_2CO_3] = 5.00x10^{-2}M, [$NaHCO_3$] = 2.00x10^{-3}M

[KCl] = 2.00x 10^{-3}M, pH = 10.8 and Temp. 30°C

μ = 17.50x10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50x10^{-3}M) in ml	10^2 ko = $\frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
10	2.04	20.40*
20	3.04	10.00
30	4.02	9.80
40	5.02	10.00
50	6.04	10.20
60	7.04	10.00
80	9.02	9.90
100	11.04	10.10
120	13.04	10.00
140	15.06	10.00

Average k_o (excluding *) = 10.00x10^{-2} ml min^{-1}

k_s = 10.00x10^{-6} mol l^{-1} min

TABLE 3.16

$[CuSO_4] = 3.00 \times 10^{-3}$ M, [D-glucose] $= 5.00 \times 10^{-2}$ M

[Free Bip] $= 5.00 \times 10^{-3}$ M, [Ir(III)] $= 5.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

[KCl] $= 2.00 \times 10^{-3}$ M, pH $= 10.8$ and Temp. 30°C

$\mu = 17.50 \times 10^{-2}$ M

Time (min.)	Volume of $K_2Cr_2O_7$ (1.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
10	1.16	3.20
20	1.50	3.40
40	2.20	3.50
60	2.88	3.40
80	3.56	3.40
100	4.28	3.60
120	4.96	3.40
140	5.62	3.30
160	6.26	3.20

Average k_o (excluding *) $= 3.38 \times 10^{-2}$ ml min^{-1}

$k_s = 10.14 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.17

$[CuSO_4] = 4.00 \times 10^{-3}$M, [D-glucose] $= 5.00 \times 10^{-2}$M

[Free Bip.] $= 5.00 \times 10^{-3}$M, [Ir(III)] $= 5.00 \times 10^{-6}$M

$[Na_2CO_3] = 5.00 \times 10^{-2}$M, $[NaHCO_3] = 2.00 \times 10^{-3}$M

[KCl] $= 2.00 \times 10^{-3}$M, pH $= 10.8$ and Temp. 30°C

$\mu = 17.50 \times 10^{-2}$M

Time (min.)	Volume of $K_2Cr_2O_7$ (1.50×10^{-3}N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
10	1.20	3.60
20	1.54	3.40
40	2.24	3.50
60	2.92	3.40
85	3.78	3.44
110	4.70	3.68
140	5.72	3.40
180	7.00	3.20
220	8.40	3.50

Average k_0 (excluding *) $= 3.46 \times 10^{-2}$ ml min^{-1}

$k_s = 10.38 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.18

$[CuSO_4] = 5.00 \times 10^{-3}M$, [D-glucose] $= 5.00 \times 10^{-2}M$

[Free Bip.] $= 5.00 \times 10^{-3}M$, $[Ir(III)] = 5.00 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 2.00 \times 10^{-3}M$

$[KCl] = 2.00 \times 10^{-3}M$, pH $= 10.8$, and Temp. 30°C

$\mu = 17.50 \times 10^{-2}M$

Time (min.)	Volume of $K_2Cr_2O_7$ ($2.00 \times 10^{-3}N$) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.04	20.80*
10	1.18	2.80
20	1.44	2.60
40	1.94	2.50
60	2.42	2.40
80	2.88	2.30
110	3.60	2.40
140	4.34	2.46
180	5.34	2.50
220	6.40	2.65

Average k_o (excluding *) $= 2.51 \times 10^{-2}$ ml min^{-1}

$k_s = 10.04 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.19

[Cu SO_4] = 1.00×10^{-3}M, [D-galactose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ir(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

μ = 17.50×10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	10^2 ko= $\frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40
10	1.64	12.40
20	2.84	12.00
30	4.06	12.20
40	5.26	12.00
50	6.48	12.22
60	7.66	11.80
70	8.82	11.60
80	9.98	11.60

Average k_o (excluding *) = 11.97×10^{-2} ml min^{-1}

k_s = 11.97×10^{-6} mol l^{-1} min^{-1}

TABLE 3.20

$[CuSO_4] = 1.25 \times 10^{-3}$M, [D - galactose] $= 5.00 \times 10^{-2}$M

[Free Bip.] $= 5.00 \times 10^{-3}$M, $[I_r(III)] = 5.00 \times 10^{-6}$M

$[Na_2CO_3] = 5.00 \times 10^{-2}$M, $[NaHCO_3] = 2.00 \times 10^{-3}$M

$[KCl] = 2.00 \times 10^{-3}$M, pH = 10.8 and Temp. 30°C

$\mu = 17.50 \times 10^{-2}$M

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}M) in ml	$10^2 k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
10	1.62	12.00
15	2.24	12.40
20	2.88	12.80
25	3.48	12.00
30	4.10	12.40
40	5.30	12.00
50	6.32	12.20
60	7.54	12.20
70	8.74	12.00
80	9.96	12.20

Average k_0 (excluding *) $= 12.22 \times 10^{-2}$ ml min^{-1}

$k_s = 12.22 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 3.21

$[Cu\ SO_4] = 2.00x10^{-3}M$, [D - galactose] = $5.00x10^{-2}M$

[Free Bip.] = $5.00x10^{-3}M$, $[I_r(III)] = 5.00x10^{-6}M$

$[Na_2CO_3] = 5.00x10^{-2}M$, $[NaHCO_3] = 2.00x10^{-3}M$

$[KCl] = 2.00x10^{-3}M$, pH = 10.8 and Temp. 30^oC

$\mu = 17.50 \times 10^{-2}M$

Time (min.)	Volume of $K_2Cr_2O_7$ $(0.50x10^{-3}N)$ in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.04	20.80*
10	1.64	12.00
20	2.84	12.00
30	4.06	12.20
40	5.30	12.24
50	6.50	12.00
60	7.74	12.40
70	8.94	12.00
80	10.16	12.20
90	11.36	12.00
100	12.60	12.40

Average k_o (excluding *) = 12.14×10^{-2} ml min^{-1}

$k_s = 12.14 \times 10^{-6}$ mol lit^{-1} min^{-1}

TABLE 3.22

[Cu SO_4] = 3.00×10^{-3}M, [D-galactose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

$\mu = 17.50 \times 10^{-2}$M

Time (min.)	Volume of $K_2Cr_2O_7$ (1.50×10^{-3}M) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.06	21.20*
10	1.26	4.00
15	1.48	4.40
20	1.68	4.00
30	2.10	4.20
40	2.52	4.20
60	3.36	4.20
80	4.16	4.00
100	5.00	4.20
120	5.80	4.00
140	6.62	4.10

Average k_o (excluding *) = 4.13×10^{-2} ml min^{-1}

$k_s = 12.39 \times 10^{-6}$ mol lit^{-1} min^{-1}

TABLE 3.23

[Cu SO_4] = 4.00×10^{-3}M, [D-galactose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

μ = 17.50×10^{-2}M

Time (min.)	Volume of $K_2Cr_2O_7$ (2.00×10^{-3}N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.04	20.80*
10	1.20	3.20
15	1.38	3.60
20	1.52	2.80
30	1.82	3.00
40	2.12	3.00
60	2.72	3.00
90	3.64	3.06
130	4.84	3.00
180	6.44	3.33
240	8.24	3.00

Average k_o (excluding *) = 3.09×10^{-2} ml min^{-1})

k_s = 12.36×10^{-6} mol l^{-1} min^{-1}

TABLE 3.24

[Cu SO_4] = 5.00×10^{-3} M, [D-galactose] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ir(III)] = 5.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 2.00×10^{-3} M, pH = 10.8 and Temp. 30°C

μ = 17.50×10^{-2} M

Time (min.)	Volume of $K_2Cr_2O_7$ (2.00×10^{-3} N) in ml	$10^2 k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.04	20.80 *
10	1.20	3.20
20	1.50	3.00
30	1.82	3.20
40	2.12	3.00
50	2.44	3.20
75	3.20	3.04
100	3.98	3.12
140	5.20	3.05
180	6.44	3.10
220	7.74	3.25

Average k_0 (excluding *) = 3.12×10^{-2} ml min^{-1}

k_0 = 12.48×10^{-6} mol l^{-1} min^{-1}

The kinetic results obtained and recorded in tables 3.1 - 3.6 and tables 3.7 - 3.12 in oxidation of glycine and alanine by Cu(II) in the presence of alkaline solution of ruthenium(III) chloride have been summarised in tables 3.25 and 3.26 respectively. The kinetic data reported in tables 3.13 - 3.18 and tables 3.19 - 3.24 in Ir(III) catalysed oxidation of D-glucose and D-galactose by Cu(II) in alkaline media have been summarised in tables 3.27 and 3.28 respectively.

TABLE 3.25

[Glycine] = 10.00×10^{-2} M, [Ru(III)] = 4.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.8, [Free Bip.] = 6.00×10^{-3} M

μ = 17.50×10^{-2} M and Temp. 30°

[$CuSO_4$] $\times 10^3$ M	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.00	6.14
1.25	6.19
2.00	6.18
3.00	6.71
4.00	6.24
5.00	6.16

TABLE 3.26

[Alanine] = 10.00×10^{-2}M, [Ru(III)] = 4.00×10^{-6}M

[Free Bip.] = 5.00×10^{-3}M, [Na_2CO_3] = 5.00×10^{-2}M

[$NaHCO_3$] = 2.00×10^{-3}M, [KCl] = 1.00×10^{-3}M,

pH = 10.9 Temp. 30°C and

μ = 17.50×10^{-2}M

[Cu SO_4] x 10^3M	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.00	4.18
1.25	4.17
2.00	4.19
3.00	4.22
4.00	4.16
5.00	4.12

TABLE 3.27

[D - glucose] = 5.00×10^{-2}M, [Ir(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8

μ = 17.50×10^{-2}M and Temp. 30°C

[Free Bip] = 5.00×10^{-3} M

[Cu SO_4] x 10^3M	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.00	10.00
1.25	10.00
2.00	10.00
3.00	10.14
4.00	10.38
5.00	10.04

TABLE 3.28

[D - galactose] = 5.00 x 10^{-2}M, [Ir(III)] = 5.00x10^{-6}M

[Na_2CO_3] = 5.00x10^{-2}M, [$NaHCO_3$] = 2.00 x 10^{-3}M

[KCl] = 2.00 x 10^{-3}M, pH = 10.8 [Free Bip] = 5.00 x 10^{-3} M

μ = 17.50 x 10^{-2}M and Temp. 10.8

[Cu SO_4] x 10^3M	k_s x 10^6 mol l^{-1} min^{-1}
1.00	11.97
1.25	12.22
2.00	12.14
3.00	12.39
4.00	12.36
5.00	12.48

An examination of kinetic data reported in tables 3.25 and 3.26 in a summarised manner in the oxidation of glycine and alanine respectively by copper sulphate in the presence of 2,2' bipyridyl and alkaline solution of ruthenium(III) chloride clearly indicates that both the processes follow zero - order kinetics in copper sulphate at different concentrations of copper sulphate.

Zero - order kinetics with respect to copper sulphate has also been observed in iridium(III) chloride catalysed oxidation of D-glucose and D-galactose by alkaline solution of copper sulphate in the presence of 2,2' bipyridyl as ks values at different concentrations of copper sulphate have been observed to be nearly constant. Thus order of all the reactions with respect to copper sulphate is zero.

CHAPTER IV

DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO AMINO ACIDS AND SUGARS IN THEIR Ru(III) AND Ir(III) CATALYSED OXIDATIONS RESPECTIVELY BY ALKALINE COPPER SULPHATE SOLUTION

4 : DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO AMINO ACIDS AND SUGARS IN THEIR OXIDATIONS CATALYSED BY Ru(III) AND Ir(III) RESPECTIVELY BY BY ALKALINE SOLUTIONS OF COPPER SULPHATE

In this chapter an effort has been made to determine the order of the reaction with respect to amino acids viz. glycine and alanine in their oxidations with copper sulphate in the presence of alkaline solution of ruthenium(III) chloride as homogeneous catalyst. Similarly an attempt has also been made to ascertain the order of the reaction with respect to sugars viz. D-glucose and D-galactose in their oxidations with alkaline solution of copper sulphate using iridium(III) chloride as homogeneous catalyst. In this chapter all the experiments have been carried out under isolation conditions i.e. the concentrations of all the reducing substrate have been maintained larger as compared to that of copper sulphate. The results of all the experiments have been recorded in tables 4.1 - 4.5, and tables 4.6 - 4.10 in oxidation of glycine and alanine, respectively and in tables 4.11 - 4.15 and tables 4.16 - 4.20 in oxidation of D-glucose and D-galactose respectively. The value

of standard zero order rate constant i.e. k_s has been calculated as usual by multiplying k_0 value with S/V where S and V have their usual meanings as described in previous chapter. In the bottom of each table the values of k_s at different concentrations of substrate have been given.

TABLE 4.1

$[Cu\ SO_4] = 1.25\times10^{-3}$M, [Glycine] $= 2.50\times10^{-2}$M

[Free Bipyridyl] $= 5.00\times10^{-3}$M, [Ru(III)] $= 4.00\times10^{-6}$M

$[Na_2CO_3] = 5.00\times10^{-2}$M, $[NaHCO_3] = 2.00\times10^{-3}$M

[KCl] $= 1.00\times10^{-3}$M pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.18	1.60
40	1.60	1.68
80	2.20	1.50
120	2.84	1.60
160	3.46	1.55
200	4.06	1.50
250	4.88	1.64
300	5.68	1.60
350	6.48	1.60

Average k_o (excluding *) $= 1.58 \times 10^{-2}$ ml min^{-1}

$k_s = 1.58\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.2

[Cu SO_4] = 1.25x10^{-3}M, [Glycine] = 5.00x10^{-2}M

[Free Bip.] = 5.00x10^{-3}M, [Ru(III)] = 4.00x10^{-6}M

[Na_2CO_3] = 5.00x10^{-2}M, [$NaHCO_3$] = 2.00x10^{-3}M

[KCl] = 1.00x10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.5 x 10^{-3}N) in ml	10^2 k_o = $\frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.04	20.80
15	1.36	3.20
30	1.86	3.33
45	2.34	3.20
60	2.82	3.20
90	3.72	3.00
120	4.72	3.33
160	5.94	3.05
200	7.24	3.25
250	8.88	3.28

Average k_o (excluding *) = 3.20 x 10^{-2} ml min^{-1}

k_s = 3.20x10^{-6} mol l^{-1} min^{-1}

TABLE 4.3

$[Cu\ SO_4] = 4.25\times10^{-3}$M, [Glycine] = 7.50×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

$[Na_2CO_3] = 5.00\times10^{-2}$M, $[NaHCO_3] = 2.00\times10^{-3}$ M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.50	5.00
25	1.98	4.80
40	2.74	5.06
60	3.74	5.00
80	4.64	4.50
100	5.68	5.05
120	6.58	4.50
140	7.50	4.60
180	8.44	4.70

Average k_o (excluding *) = 4.80×10^{-2} ml/min^{-1}

$k_s = 4.80\times10^{-6}$ mol l^{-} min^{-1}

TABLE 4.4

$[Cu\ SO_4] = 1.25x10^{-3}M$, $[Glycine] = 12.50x10^{-2}M$

$[Free\ Bip.] = 5.00x10^{-3}M$, $[Ru(III)] = 4.00x10^{-6}M$

$[Na_2CO_3] = 5.00x10^{-2}M$, $[NaHCO_3] = 2.00x10^{-3}M$

$[KCl] = 1.00x10^{-3}M$, pH = 10.8 and Temp. $30^{\circ}C$

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50x10^{-3}$ N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.82	8.00
25	2.58	7.60
40	3.76	7.46
60	5.36	8.00
80	5.86	7.50
100	7.38	7.60
120	8.88	7.50
140	10.42	7.70

Average k_o (excluding *) = $7.68x10^{-2}$ ml min^{-1}

$k_s = 7.68x10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.5

$[Cu\ SO_4] = 1.25x10^{-3}M$, $[Glycine] = 15.00x10^{-2}M$

$[Free\ Bip.] = 5.00x10^{-3}M$, $[Ru(III)] = 4.00x10^{-6}M$

$[Na_2CO_3] = 5.00x10^{-2}M$, $[NaHCO_3] = 2.00x10^{-3}M$

$[KCl] = 1.00x10^{-3}M$, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50x10^{-3}N$) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
15	1.94	9.40
25	2.90	9.60
40	4.32	9.46
55	5.68	9.01
70	7.08	9.33
85	8.50	9.46
100	9.98	9.86
120	11.98	10.00

Average k_o (excluding *) = 9.52×10^{-2} ml min^{-1}

$k_s = 9.52x10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.6

[Cu SO_4] = 1.00×10^{-3}M, [Alanine] = 2.50×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
20	1.16	1.06
35	1.34	1.20
60	1.60	1.04
100	2.00	1.00
150	2.56	1.12
200	3.16	1.20
250	3.72	1.12
300	4.30	1.16
360	4.96	1.10
420	5.60	1.06

Average k_0 (excluding *) = 1.11×10^{-2} ml min^{-1}

k_s = 1.11×10^{-6} mol l^{-1} min^{-1}

TABLE 4.7

$[CuSO_4] = 1.00\times10^{-3}M$, $[\text{Alanine}] = 5.00\times10^{-2}M$

$[\text{Free Bip.}] = 5.00\times10^{-3}M$, $[\text{Ru(III)}] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, pH = 10.8 and Temp. 30°C

$[NaHCO_3] = 2.00\times10^{-3}M$, $[KCl] = 1.00\times10^{-3}M$

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.22	2.20
30	1.56	2.26
45	1.88	2.13
60	2.22	2.26
80	2.68	2.30
100	3.12	2.20
140	3.94	2.05
180	4.80	2.15
220	5.60	2.00
260	6.44	2.10

Average k_0 (excluding *) = 2.16×10^{-2} ml min^{-1}

$k_s = 2.16\times10^{-5}$ mol l^{-1} min^{-1}

TABLE 4.8

[Cu SO_4] = 1.00×10^{-3} M, [Alanine] = 7.50×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ru(III)] = 4.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.36	3.40
25	1.70	3.40
35	2.02	3.20
50	2.52	3.33
65	3.06	3.60
80	3.54	3.20
100	4.22	3.40
120	4.88	3.30
140	5.58	3.50
160	6.26	3.40

Average k_o (excluding *) = 3.37×10^{-2} ml min^{-1}

$k_p = 3.37 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.9

[Cu SO_4] = 1.00×10^{-3}N, [Alanine] = 12.50×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and Temp. 30^{0}C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.04	20.80*
15	1.58	5.40
25	2.14	5.60
35	2.66	5.20
50	3.46	5.33
70	4.56	5.50
90	5.60	5.20
110	6.66	5.30
130	7.76	5.50
150	8.84	5.40
170	9.94	5.50

Average k_0 (excluding *) = 5.39×10^{-2} ml min^{-1}

$k_s = 5.39 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.10

$[\mathrm{Cu\ SO_4}] = 1.00\times10^{-3}$M, $[\mathrm{Alanine}] = 15.00\times10^{-2}$M

$[\mathrm{Free\ Bip.}] = 5.00\times10^{-3}$M, $[\mathrm{Ru(III)}] = 4.00\times10^{-6}$M

$[\mathrm{Na_2CO_3}] = 5.00\times10^{-2}$M, $[\mathrm{NaHCO_3}] = 2.00\times10^{-3}$M

$[\mathrm{KCl}] = 1.00\times10^{-3}$M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.70	6.80
25	2.36	6.60
35	3.04	6.80
45	3.68	6.40
60	4.68	6.66
75	5.70	6.80
115	6.68	6.53
130	7.64	6.40
160	8.66	6.80

Average k_o (excluding *) = 6.58×10^{-2} ml min^{-1}

$k_s = 6.58\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.11

$[CuSO_4] = 1.25\times10^{-3}M$, [D-glucose] $= 2.50\times10^{-2}M$

[Free Bip.] $= 5.00\times10^{-3}M$, $[Ir(III)] = 5.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 2.00\times10^{-3}M$, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.04	20.80*
15	1.56	5.20
25	2.10	5.40
35	2.60	5.00
45	3.12	5.20
60	3.88	5.06
75	4.66	5.20
90	5.42	5.06
110	6.42	5.00
130	7.44	5.10
150	8.44	5.00

Average k_o (excluding *) $= 5.12\times10^{-2}$ ml min^{-1}

$k_s = 5.12\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.12

$[CuSO_4] = 1.25\times10^{-3}$N, [D-glucose] $= 7.50\times10^{-2}$M

[Free Bip.] $= 5.00\times10^{-3}$M, [Ir(III)] $= 5.00\times10^{-6}$M

$[Na_2CO_3] = 5.00\times10^{-2}$M, $[NaHCO_3] = 2.00\times10^{-3}$M

[KCl] $= 2.00\times10^{-3}$M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	2.48	14.60
25	4.00	15.20
35	5.50	15.00
45	7.52	15.20
55	9.00	14.80
65	10.44	14.40
75	11.94	15.00

Average k_o (excluding *) $= 14.88\times10^{-2}$ ml min^{-1}

$k_s = 14.88 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.13

$[Cu\ SO_4] = 1.25 \times 10^{-3}M$, [D-glucose] $= 10.00 \times 10^{-2}M$

[Free Bip.] $= 5.00 \times 10^{-3}M$, $[I_r(III)] = 5.00 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 2.00 \times 10^{-3}M$

[KCl] $= 2.00 \times 10^{-3}M$, pH = 10.8 and Temp. $30^{0}C$

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50 \times 10^{-3}N$) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml /min
0	0.00	--
5	1.02	20.40*
10	2.02	20.00
15	3.04	20.40
20	4.04	20.00
25	5.08	20.80
30	6.06	19.60
35	7.06	20.00
40	8.08	20.40
45	9.10	20.40
50	10.10	20.00

Average $k_o = 20.20 \times 10^{-2}$ ml min^{-1}

$k_s = 20.20 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.14

[Cu SO_4] = 1.25×10^{-3}M, [D-glucose] = 12.50×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ir(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
10	2.26	24.80
15	3.52	25.20
20	4.78	25.20
25	6.02	24.80
30	7.26	24.80
35	8.52	25.20
40	9.78	25.20
45	11.00	24.40
50	12.26	25.20

Average k_o (excluding *) = 24.98×10^{-2} ml min^{-1}

$k_s = 24.98 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.15

$[Cu\ SO_4] = 1.25 \times 10^{-3}$ M, $[D - glucose] = 15.00 \times 10^{-2}$ M

$[Free\ Bip.] = 5.00 \times 10^{-3}$ M, $[I_r(III)] = 5.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

$[KCl] = 2.00 \times 10^{-3}$ M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
10	2.50	30.00
15	4.00	30.00
20	5.46	29.20
25	7.00	30.80
30	8.48	29.60
35	10.00	30.40
40	11.50	30.00

Average k_o (excluding *) = 30.00×10^{-2} ml min^{-1}

$k_s = 30.00 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.16

[Cu SO_4] = 1.00×10^{-3}N [D-galactose] = 2.50×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.62	6.00
25	2.24	6.20
35	2.84	6.00
45	3.48	6.40
55	4.08	6.00
65	4.68	6.00
75	5.30	6.20
90	6.20	6.00
110	7.44	6.20

Average k_0 (excluding *) = 6.11×10^{-2} ml min^{-1}

k_0 = 6.11×10^{-6} mol l^{-1} min^{-1}

TABLE 4.17

$[Cu\ SO_4] = 1.00\times10^{-3}$N, [D-galactose] $= 7.50\times10^{-2}$M

[Free Bip.] $= 5.00\times10^{-3}$M, $[I_r(III)] = 5.00\times10^{-6}$M

$[Na_2CO_3] = 5.00\times10^{-2}$M, $[NaHCO_3] = 2.00\times10^{-3}$M

[KCl] $= 2.00\times10^{-3}$M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
10	1.90	18.00
15	2.82	18.40
20	3.72	18.00
25	4.64	18.40
30	5.52	17.60
35	6.42	18.00
40	7.34	18.40
45	8.28	18.80
50	9.18	18.00

Average k_o (excluding *) $= 18.36 \times 10^{-2}$ ml min^{-1}

$k_s = 13.36 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.19

$[Cu\,SO_4] = 1.00 \times 10^{-3}M$, $[\text{D-galactose}] = 10.00 \times 10^{-2}M$

$[\text{Free Bip.}] = 5.00 \times 10^{-3}M$, $[Ir(III)] = 5.00 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 2.00 \times 10^{-3}M$

$[KCl] = 2.00 \times 10^{-3}M$, pH = 10.3 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50 \times 10^{-3}N$) in ml	$10^2\,k_O = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
10	2.20	24.00
15	3.22	24.40
20	4.40	23.60
25	5.60	24.00
30	6.82	24.40
35	8.00	23.60
40	9.22	24.40

Average k_O (excluding *) = 24.05×10^{-2} ml min^{-1}

$k_S = 24.05 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.19

$[CuSO_4] = 1.00 \times 10^{-3}$ M, $[\text{D-galactose}] = 12.50 \times 10^{-2}$ M

$[\text{Free Bip}] = 5.00 \times 10^{-3}$ M, $[Ir(III)] = 5.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.0 \times 10^{-3}$ M

$[KCl] = 2.00 \times 10^{-3}$ M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	10^2 $k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
10	2.50	30.00
15	4.00	30.00
20	5.48	29.60
25	7.00	30.40
30	8.46	29.20
35	10.96	30.00

Average k_o (excluding *) = 29.86×10^{-2} ml min^{-1}

$k_s = 29.86 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 4.20

[Cu SO_4] = 1.00×10^{-3}M, [D-galactose] = 15.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}M) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
8	2.08	35.00
12	3.52	36.00
15	4.62	36.66
18	5.70	36.00
21	6.80	36.66
24	7.90	36.66
27	8.98	36.00
30	9.98	33.33

Average k_o (excluding *) = 35.91×10^{-2} ml min^{-1}

k_s = 35.91×10^{-6} mol l^{-1} min^{-1}

The kinetic data collected in tables 4.1 - 4.5 and tables 3.2, tables 4.6 - 4.10 and table 3.7, tables 4.11 - 4.15 and table 3.14 and tables 4.16-4.20 and table 3.19 have been summarised in tables 4.21, 4.22, 4.23 and table 4.24 respectively.

TABLE 4.21

[Cu SO_4] = 1.25×10^{-3}M, [Free Bip.] = 5.00×10^{-3}M

[Ru(III)] = 4.00×10^{-6}M, [KCl] = 1.00×10^{-3}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

pH = 10.8 and Temp. 30°C

[Glycine] x 10^2 M	$k_s \times 10^6$ mol l^{-1} min^{-1}	$k_1 \times 10^5$ min^{-1}
2.50	1.58	6.32
5.00	3.20	6.40
7.50	4.80	6.40
10.00	6.19	6.19
12.50	7.68	6.14
15.00	9.52	6.35

TABLE 4.22

$[Cu\ SO_4] = 1.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$

$[Free\ Bip.] = 5.00\times10^{-3}M$, $[KCl] = 1.00\times10^{-3}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

pH = 10.8 and Temp. 30°C

[Alanine] x 10^2	$k_s \times 10^6$ mol l^{-1} min^{-1}	$k_1 \times 10^5$ min^{-1}
2.50	1.11	4.40
5.00	2.16	4.32
7.50	3.37	4.40
10.00	4.18	4.18
12.50	5.39	4.32
15.00	6.58	4.38

TABLE 4.23

$[Cu\ SO_4] = 1.25 \times 10^{-3}$ M, $[Ir(III)] = 5.00 \times 10^{-6}$ M

$[Free\ Bip.] = 5.00 \times 10^{-3}$ M, $[KCl] = 2.00 \times 10^{-3}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

pH = 10.8 and Temp. 30°C

[D-glucose] x 10^2	$k_s \times 10^6$ mol l^{-1} min^{-1}	$k_1 \times 10^4$ min^{-1}
2.50	5.12	2.04
5.00	10.00	2.00
7.50	14.88	1.98
10.00	20.20	2.02
12.50	24.98	1.99
15.00	30.00	2.00

TABLE 4.24

[Cu SO_4] = 1.00×10^{-3}M, [Free Bip.] = 5.00×10^{-3}M

[Ir(III)] = 5.00×10^{-6}M, [KCl] = 2.00×10^{-3}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

pH = 10.8 and Temp. 30°C

[D-galactose] x 10^2 M	$k_s \times 10^6$ mol l^{-1} min^{-1}	$k_1 \times 10^4$ min^{-1}
2.50	6.11	2.44
5.00	11.97	2.39
7.50	18.36	2.44
10.00	24.05	2.41
12.50	29.86	2.39
15.00	35.91	2.39

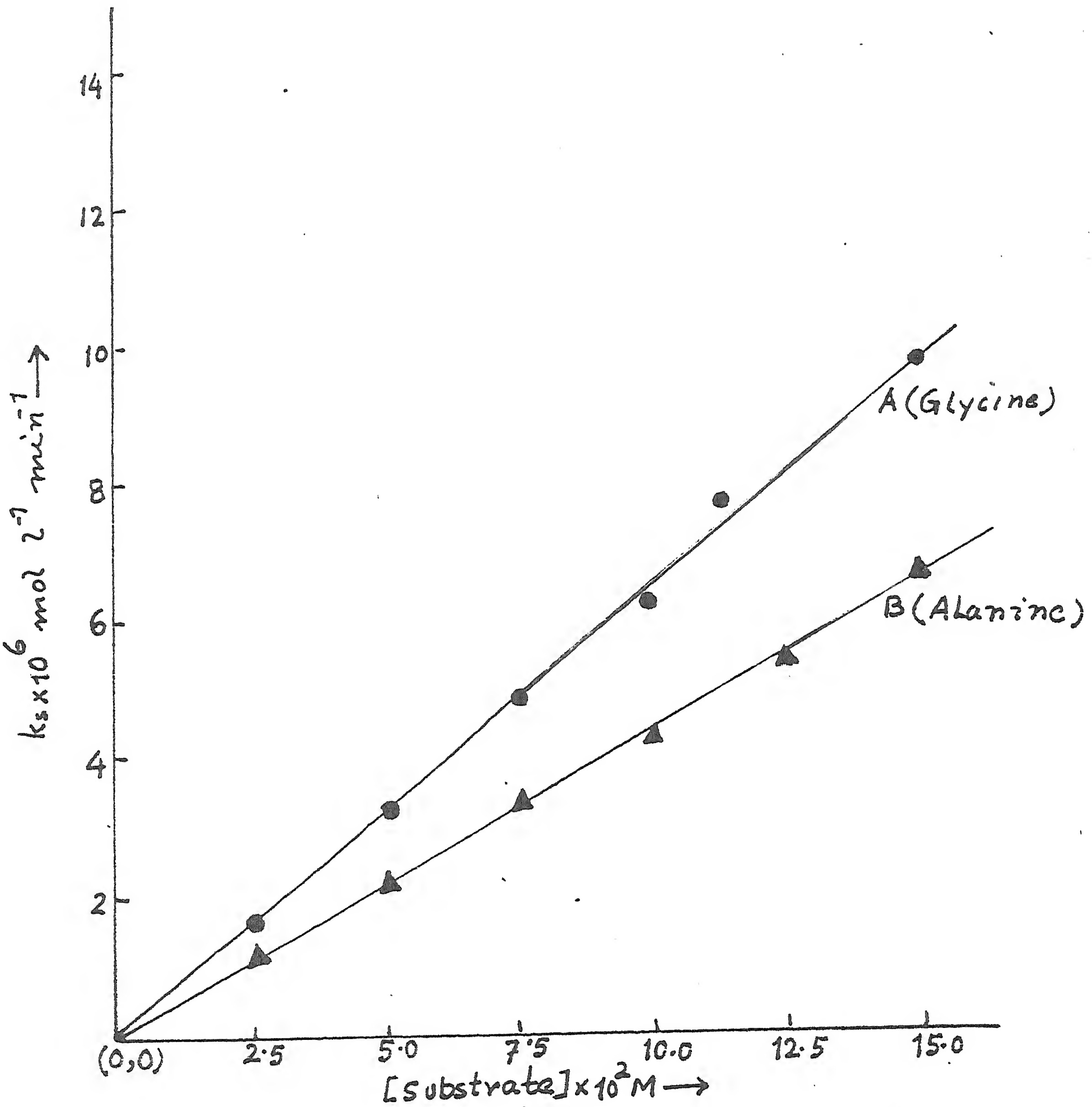

FIG. 4.1: PLOT BETWEEN k_s AND [SUBSTRATE] AT 30°C

$[CuSO_4] = 1{\cdot}25$ (A) AND $1{\cdot}00$ (B) $\times 10^{-3}$ M, $[Ru(III)] = 4{\cdot}00 \times 10^{-6}$ M,

[Free BIPYRIDYL] $= 5{\cdot}00 \times 10^{-3}$ M, $[Na_2CO_3] = 5{\cdot}00 \times 10^{-2}$ M,

$[NaHCO_3] = 2{\cdot}00 \times 10^{-3}$ M, $[KCl] = 1{\cdot}00 \times 10^{-3}$ M, pH = 10.80

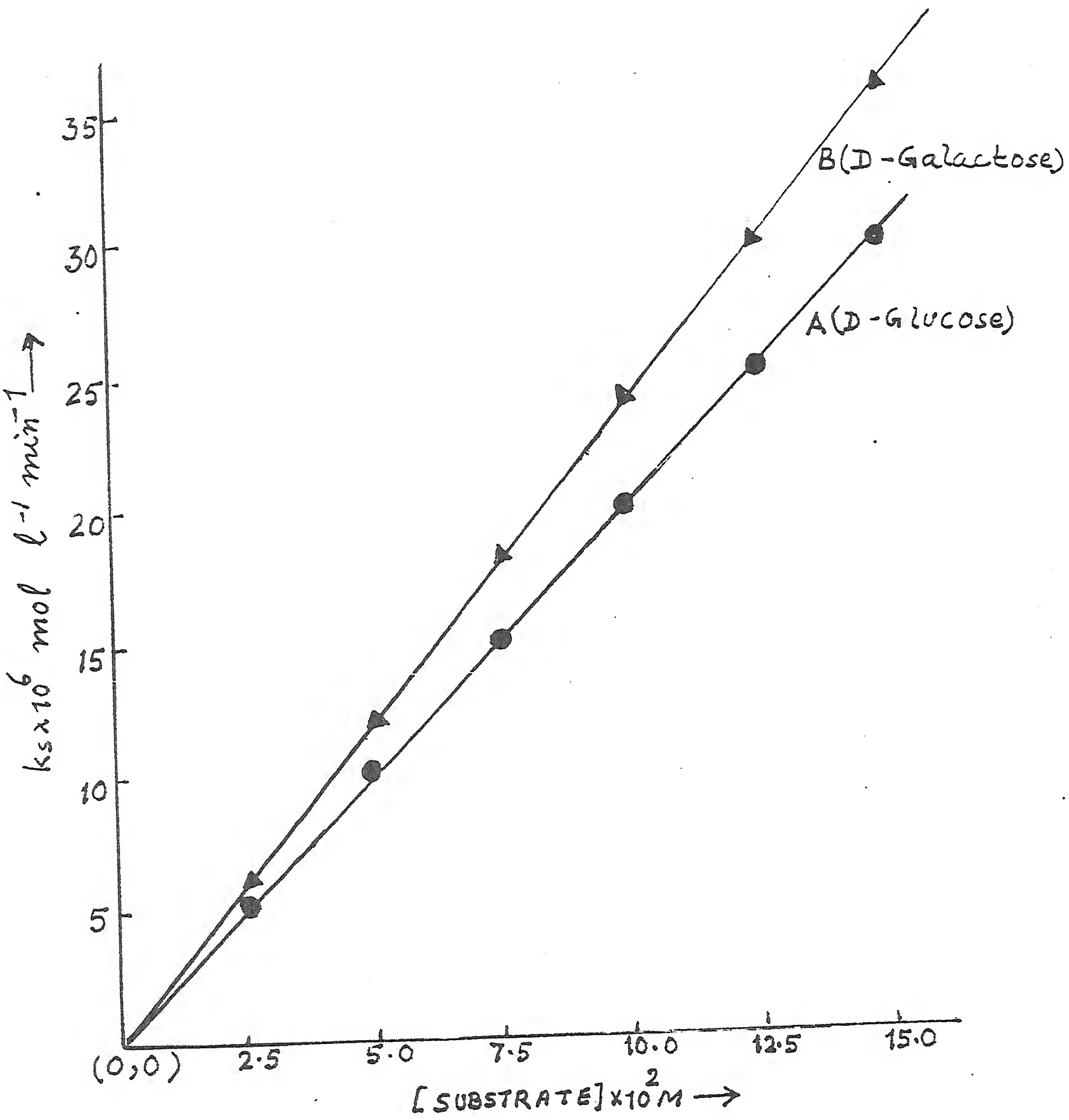

FIG. 4.2 : PLOT BETWEEN k_s AND [SUBSTRATE] AT 30°C
$[CuSO_4]$ = 1.50 (A) AND 1.00 (B) $\times 10^{-3}$ M, [Ir(III)] = 5.00×10^{-6} M,
[FREE BIPYRIDYL] = 5.00×10^{-3} M, [KCl] = 2.00×10^{-3} M, pH = 10.80
$[Na_2CO_3]$ = 5.00×10^{-2} M AND $[NaHCO_3]$ = 2.00×10^{-3} M

A close examination of data of tables 4.21, 4.22, 4.23 and 4.24 clearly indicates that on increasing the concentration of reducing amino acids and sugars the corresponding values of k_s also increase in direct proportionality showing thus first - order in amino acids and sugars. This is also obvious from constant k_1 values in each tables described above.

A straight line with slope equal to k_1 values is obtained in each case when k_s values are plotted against concentration of eahh of glycine, alanine, D-glucose and D-galactose (Fig. 4.1 & 4.2). Thus fair degree of closeness in k_1 value and corresponding slope in oxidation of each of glycine, alanine, D-glucose and D-galactose confirms first - order kinetics in reducing amino acids and sugars.

CHAPTER V

DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO Ru(III) IN OXIDATION OF AMINO ACIDS AND WITH RESPECT TO Ir(III) IN OXIDATION OF SUGARS BY ALKALINE SOLUTION OF COPPER SULPHATE

5 : DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO Ru(III) IN OXIDATION OF AMINO ACIDS AND WITH RESPECT TO Ir(III) IN OXIDATION OF SUGARS BY ALKALINE SOLUTION OF COPPER SULPHATE

The main aim of various experiments performed here in this chapter is to determine the order of oxidation of amino acids and sugars by copper sulphate with respect to catalyst i.e. Ru(III) and Ir(III) respectively. In order to do so, various experiments with varying concentrations of Ru(III) in oxidation of amino acids viz., glycine and alanine and similarly a set of experiments containing different concentrations of Ir(III) in oxidation of sugars i.e. D-glucose and D-galactose but at fixed concentrations of all other reactants have been performed. The results of such experiments have been recorded in tables 5.1 - 5.5, and tables 5.6 -5.10 in oxidation of glycine and alanine respectively and in tables 5.11 - 5.15 and tables 5.16 - 5.20 in oxidation of D-glucose and D-galactose, respectively. Here also the value of ($-dc/dt$) i.e. standard zero order rate constant (k_0) has been determined by following the same procedure as described in 3rd chapter.

TABLE 5.1

$[Cu\ SO_4] = 1.25 \times 10^{-3} M$, $[Glycine] = 5.00 \times 10^{-}$

$[Free\ Bip.] = 5.00 \times 10^{-3} M$, $[Ru(III)] = 2.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 2.00 \times 10^{-3} M$

$[KCl] = 1.00 \times 10^{-3} M$, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2 Cr_2 O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.16	1.60
25	1.32	1.60
40	1.58	1.60
60	1.88	1.50
90	2.38	1.66
140	3.16	1.56
200	4.16	1.66
260	5.12	1.60
320	6.02	1.50
380	6.94	1.53

Average k_o (excluding *) = 1.58×10^{-2} ml min^{-1}

$k_s = 1.58 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.2

$[Cu\ SO_4] = 1.25 \times 10^{-3}$ M, [Glycine] $= 5.00 \times 10^{-2}$ M

[Free Bip.] $= 5.00 \times 10^{-3}$ M, [Ru(III)] $= 3.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

[KCl] $= 1.00 \times 10^{-3}$ M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.26	2.40
30	1.60	2.26
50	2.08	2.40
75	2.70	2.48
100	3.30	2.40
140	4.24	2.35
180	5.20	2.40
220	6.18	2.45
280	7.58	2.33
240	9.08	2.50

Average k_o (excluding *) $= 2.40 \times 10^{-2}$ ml min^{-1}

$k_s = 2.40 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.3

[Cu SO_4] = 1.25×10^{-3} M, [Glycine] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ru(III)] = 5.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
15	1.38	3.80
25	1.78	4.00
40	2.34	3.73
60	3.12	3.90
90	4.28	3.86
120	5.42	3.80
150	6.58	3.86
180	7.70	3.73
210	8.84	3.80
250	10.34	3.75

Average k_o (excluding *) = 3.82×10^{-2} ml min^{-1}

k_s = 3.82×10^{-6} mol l^{-1} min^{-1}

TABLE 5.4

$[Cu\ SO_4] = 1.25 \times 10^{-3}$M, [Glycine] $= 5.00 \times 10^{-2}$M

[Free Bip.] $= 5.00 \times 10^{-3}$M, [Ru(III)] $= 6.00 \times 10^{-6}$M

$[Na_2CO_3] = 5.00 \times 10^{-2}$M, $[NaHCO_3] = 2.00 \times 10^{-3}$M

[KCl] $= 1.00 \times 10^{-3}$M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2\ Cr_2\ O_7$ $(0.50 \times 10^{-3}$ N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.50	5.00
25	2.00	5.00
40	2.70	4.66
60	3.60	4.50
80	4.52	4.60
100	5.46	4.70
120	6.42	4.80
140	7.40	4.90
180	9.30	4.75
220	11.30	5.00

Average k_o (excluding *) $= 4.79 \times 10^{-2}$ ml min^{-1}

$k_s = 4.79 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.5

$[Cu\ SO_4] = 4.25 \times 10^{-3}M$, [Glycine] $= 5.00\times10^{-2}M$

[Free Bip.] $= 5.00\times10^{-3}M$, $[Ru(III)] = 8.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.62	6.00
25	2.24	6.20
35	2.90	6.40
45	3.50	6.00
60	4.42	6.13
75	5.36	6.26
100	6.80	5.76
125	8.30	6.00
150	9.90	6.40
175	11.42	6.08

Average k_o (excluding *) $= 6.12 \times 10^{-2}$ ml min^{-1}

$k_s = 6.12 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.6

[Cu SO_4] = 1.00x10^{-3}N, [Alanine] = 5.00x10^{-2}M

[Free Bip.] = 5.00x10^{-3}M, [Ru(III)] = 1.50x10^{-6}M

[Na_2CO_3] = 5.00x10^{-2}M, [$NaHCO_3$] = 2.00x10^{-3}M

[KCl] = 1.00x10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50x10^{-3}N) in ml	10^2 k_o = $\frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
25	1.18	0.80
60	1.46	0.80
120	1.92	0.77
180	2.36	0.73
240	2.82	0.76
300	3.30	0.80
360	3.76	0.76
420	4.20	0.73
480	4.66	0.76
540	5.12	0.76

Average k_o (excluding *) = 0.77x10^{-2} ml min^{-1}

k_s = 0.77 x 10^{-6} mol l^{-1} min^{-1}

TABLE 5.7

[Cu SO_4] = 4.00×10^{-3} M, [Alanine] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ru(III)] = 3.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
15	1.16	1.60
35	1.46	1.50
60	1.80	1.36
90	2.26	1.53
130	2.86	1.50
180	3.64	1.56
240	4.56	1.53
300	5.46	1.50
360	6.34	1.47
420	7.24	1.50

Average k_o (excluding *) = 1.51×10^{-2} ml min^{-1}

$k_s = 1.51 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.8

[Cu SO_4] = 1.00×10^{-3} M, [Alanine] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ru(III)] = 5.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.28	2.60
35	1.82	2.70
60	2.50	2.72
90	3.28	2.60
120	4.08	2.66
150	4.84	2.53
180	5.62	2.60
220	6.70	2.70
280	8.30	2.66
340	9.88	2.63

Average k_o (excluding *) = 2.64×10^{-2} ml min^{-1}

k_s = 2.64×10^{-6} mol l^{-1} min^{-1}

TABLE 5.9

$[CuSO_4] = 1.00 \times 10^{-3}$ M, [Alanine] $= 5.00 \times 10^{-2}$ M

[Free Bip.] $= 5.00 \times 10^{-3}$ M, [Ru(III)] $= 6.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

$[KCl] = 1.00 \times 10^{-3}$ M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.32	3.20
35	1.92	3.00
60	2.68	3.04
100	3.96	3.20
140	5.20	3.10
180	6.46	3.15
220	7.74	3.20
260	9.02	3.20

Average k_o (excluding *) $= 3.14 \times 10^{-2}$ ml min^{-1}

$k_s = 3.14 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.10

$[Cu\ SO_4] = 1.00\times10^{-3}$M, $[Alanine] = 5.00\times10^{-2}$M

$[Free\ Bip.] = 5.00\times10^{-3}$M, $[Ru(III)] = 7.50\times10^{-6}$M

$[Na_2CO_3] = 5.00\times10^{-2}$M, $[NaHCO_3] = 2.00\times10^{-3}$M

$[KCl] = 1.00\times10^{-3}$M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} M) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.04	20.80*
15	1.42	3.80
25	1.78	3.60
35	2.18	4.00
45	2.58	4.00
60	3.16	3.86
90	4.26	3.66
120	5.36	4.33
150	6.76	4.00
180	7.94	3.90

Average k_o (excluding *) = 3.91×10^{-2} ml min^{-1}

$k_s = 3.91 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.11

$[Cu\ SO_4] = 1.25\times10^{-3}M$, [D-glucose] $= 5.00\times10^{-2}M$

[Free Bip.] $= 5.00\times10^{-3}M$, $[I_r(III)] = 1.50\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 2.00\times10^{-3}M$, pH = 10.8 and Temp. $30^{o}C$

Time (min.)	Volume of $K_2 Cr_2 O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40
15	1.32	3.00
25	1.64	3.20
35	1.94	3.00
45	2.24	3.00
60	2.70	3.06
80	3.32	3.10
100	3.94	3.10
140	5.14	3.00
180	6.36	3.05
220	7.60	3.10

Avarage k_o (excluding *) $= 3.06 \times 10^{-2}$ ml min^{-1}

$k_s = 3.06 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.12

$[Cu\ SO_4] = 1.25 \times 10^{-3}$ M, $[\text{D-glucose}] = 5.00 \times 10^{-2}$ M

$[\text{Free Bip.}] = 5.00 \times 10^{-3}$ M, $[Ir(III)] = 3.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

$[KCl] = 2.00 \times 10^{-3}$ M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2\ Cr_2\ O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.62	6.00
25	2.24	6.20
35	2.84	6.00
45	3.44	6.00
60	4.36	6.01
80	5.58	6.10
100	6.78	6.00
120	8.00	6.10
140	9.24	6.20

Average k_0 (excluding *) = 6.07×10^{-2} ml min^{-1}

$k_s = 6.07 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.13

$[CuSO_4] = 1.25\times10^{-3}M$, $[D\text{-glucose}] = 5.00\times10^{-2}M$

$[\text{Free Bip.}] = 5.00\times10^{-3}M$, $[I_r(III)] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 2.00\times10^{-3}M$, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
15	1.82	8.20
25	2.62	8.00
35	3.40	7.80
45	4.20	8.00
60	5.42	8.13
75	6.60	7.86
90	7.80	8.00
120	10.24	8.13

Average k_o (excluding *) = 8.11×10^{-2} ml min^{-1}

$k_s = 8.11\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.14

[Cu SO_4] = 1.25×10^{-3} M, [D-glucose] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ir(III)] = 6.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 2.00×10^{-3} M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} M) in ml	10^2 $k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40
10	1.62	12.00
15	2.24	12.40
20	2.84	12.00
30	4.02	12.20
40	5.24	12.20
50	6.36	12.20
60	7.56	12.00
70	8.78	12.20
80	9.90	12.00

Average k_o (excluding *) = 12.01×10^{-2} ml min^{-1}

k_s = 12.01×10^{-6} mol l^{-1} min^{-1}

TABLE 5.15

$[Cu\ SO_4] = 1.25 \times 10^{-3}$ M, [D-glucose] $= 5.00 \times 10^{-2}$ M

[Free Bip.] $= 5.00 \times 10^{-3}$ M, $[Ir(III)] = 7.50 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

$[KCl] = 2.00 \times 10^{-3}$ M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00
15	2.50	15.00
25	4.02	15.20
35	5.52	15.00
45	7.02	15.00
55	8.54	15.20
65	10.06	15.20
75	11.56	15.00

Average k_o (excluding *) $= 15.08 \times 10^{-2}$ ml min^{-1}

$k_s = 15.08 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.16

$[CuSO_4] = 1.25\times10^{-3}$ M, [D-galactose] $= 5.00\times10^{-2}$ M

[Free Bip.] $= 5.00\times10^{-3}$ M, $[Ir(III)] = 1.50\times10^{-6}$ M

$[Na_2CO_3] = 5.00\times10^{-2}$ M, $[NaHCO_3] = 2.00\times10^{-3}$ M

$[KCl] = 2.00\times10^{-3}$ M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.04	20.80*
15	1.38	3.40
25	1.74	3.60
40	2.26	3.46
60	3.00	3.70
90	4.12	3.73
120	5.20	3.60
160	6.66	3.65
200	8.10	3.61
250	9.90	3.60

Average k_o (excluding *) $= 3.60\times10^{-2}$ ml min^{-1}

$k_s = 3.60\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 5.17

[Cu SO_4] = 4.25×10^{-3}M, [D-galactose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 3.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.76	7.40
25	2.48	7.20
35	3.22	7.40
45	3.94	7.20
60	5.00	7.06
75	6.08	7.20
90	7.18	7.33
105	8.24	7.06
120	9.32	7.20
140	10.78	7.30

Average k_o (excluding *) = 7.24×10^{-2} ml min^{-1}

k_s = 7.24×10^{-6} mol l^{-1} min^{-1}

TABLE 5.18

[Cu SO_4] = 1.25×10^{-3}M, [D-galactose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ir(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	10^2 ko = $\frac{\Delta x}{\Delta t}$ ml /min
0	0.00	- -
5	1.00	20.00*
15	1.98	9.80
25	2.94	9.60
35	3.88	9.40
45	4.84	9.60
60	6.32	9.86
75	7.76	9.60
90	8.18	9.46
105	9.62	9.60
120	11.06	9.60

Average ko (excluding *) = 9.61×10^{-2} ml min^{-1}

k_s = 9.61×10^{-6} mol l^{-1} min^{-1}

TABLE 5.19

[Cu SO_4] = 1.25×10^{-3} M, [D-galactose] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [I_r(III)] = 6.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 2.00×10^{-3} M, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
10	1.72	14.40
15	2.46	14.80
20	3.16	14.00
25	3.88	14.40
30	4.60	14.40
35	5.30	14.00
45	6.72	14.20
55	8.12	14.00
65	9.54	14.20
75	10.94	14.00

Average k_o (excluding *) = 14.24×10^{-2} ml min^{-1}

k_s = 14.24×10^{-6} mol l^{-1} min^{-1}

TABLE 5.20

$[CuSO_4] = 1.25 \times 10^{-3}M$, [D-galactose] $= 5.00 \times 10^{-2}M$

[Free Bip.] $= 5.00 \times 10^{-2}M$, $[Ir(III)] = 7.50 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 2.00 \times 10^{-3}M$

$[KCl] = 2.00 \times 10^{-2}M$, pH = 10.8 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50 \times 10^{-3}N$) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
10	1.90	18.00
15	2.92	18.90
20	3.82	18.00
25	4.68	17.20
30	5.56	17.60
35	6.44	17.60
40	7.34	18.00
45	8.22	17.60
50	9.10	17.60
60	10.84	17.40

Average k_o (excluding *) $= 17.74 \times 10^{-2}$ ml min^{-1}

$k_s = 17.74 \times 10^{-6}$ mol l^{-1} min^{-1}

The results of tables 5.1 - 5.55 & table 4.2, tables 5.6 - 5.10 and table 5.7, tables 5.11 - 5.15 & table 3.14 and tables 5.16 - 5.20 & table 3.20 have been summarised in tables 5.21, 5.21, 5.22 and 5.23 respectively.

TABLE 5.21

$[Cu\ SO_4] = 1.25 \times 10^{-3}M$, $[Glycine] = 5.00 \times 10^{-2}M$

$[Free\ Bip.] = 5.00 \times 10^{-3}M$, $[Na_2CO_3] = 5.00 \times 10^{-2}M$

$[NaHCO_3] = 2.00 \times 10^{-3}M$, $[KCl] = 1.00 \times 10^{-3}M$,

pH = 10.8 and Temp. 30°C

$[Ru(III)] \times 10^6 M$	$k_s \times 10^6$ mol l^{-1} min^{-1}	k_1 min^{-1}
2.00	1.58	0.79
3.00	2.40	0.80
4.00	3.20	0.80
5.00	3.82	0.76
6.00	4.79	0.79
8.00	6.12	0.76

Average k_1 = 0.79 min^{-1}

TABLE 5.22

$[CuSO_4] = 1.00\times10^{-3}M$, $[\text{Alanine}] = 5.00\times10^{-2}M$

$[\text{Free Bip.}] = 5.00\times10^{-3}M$, $[Na_2CO_3] = 5.00\times10^{-2}M$

$[NaHCO_3] = 2.00\times10^{-3}M$, $[KCl] = 1.00\times10^{-3}M$

pH = 10.8 and Temp. 30°C

$[Ru(III)]\times10^{6}M$	$k_s\times10^{6}$ mol l^{-1} min^{-1}	k_1, min^{-1}
1.50	0.77	0.52
3.00	1.51	0.50
4.00	2.16	0.54
5.00	2.64	0.53
6.00	3.14	0.52
7.50	3.91	0.52

Average $k_1 = 0.52$ min^{-1}

TABLE 5.23

[Cu SO_4] = 1.25×10^{-3}M, [D-glucose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Na_2CO_3] = 5.00×10^{-2}M

[$NaHCO_3$] = 2.00×10^{-3}M, [KCl] = 2.00×10^{-3}M

pH = 10.8 and Temp. 39°C

[I_r(III)] $\times 10^6$M	$k_s \times 10^6$ mol l^{-1} min^{-1}	k_1, min^{-1}
1.50	3.06	2.04
3.00	6.07	2.02
4.00	8.11	2.03
5.00	10.00	2.00
6.00	12.01	2.00
7.50	15.08	2.01

Average k_1 = 2.01 min^{-1}

TABLE 5.24

[Cu SO_4] = 1.25×10^{-3} M, [D-galactose] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Na_2CO_3] = 5.00×10^{-2} M

[$NaHCO_3$] = 2.00×10^{-3} M, [KCl] = 2.00×10^{-3} M

pH = 10.8 and Temp. 30°C

[$Ir(III)$] x 10^6 M	$k_s \times 10^6$ mol l^{-1} min^{-1}	k_1 min^{-1}
1.50	3.60	2.40
3.00	7.24	2.41
4.00	9.61	2.40
5.00	12.22	2.44
6.00	14.24	2.37
7.50	17.74	2.36

Average k_s = 2.39 min^{-1}

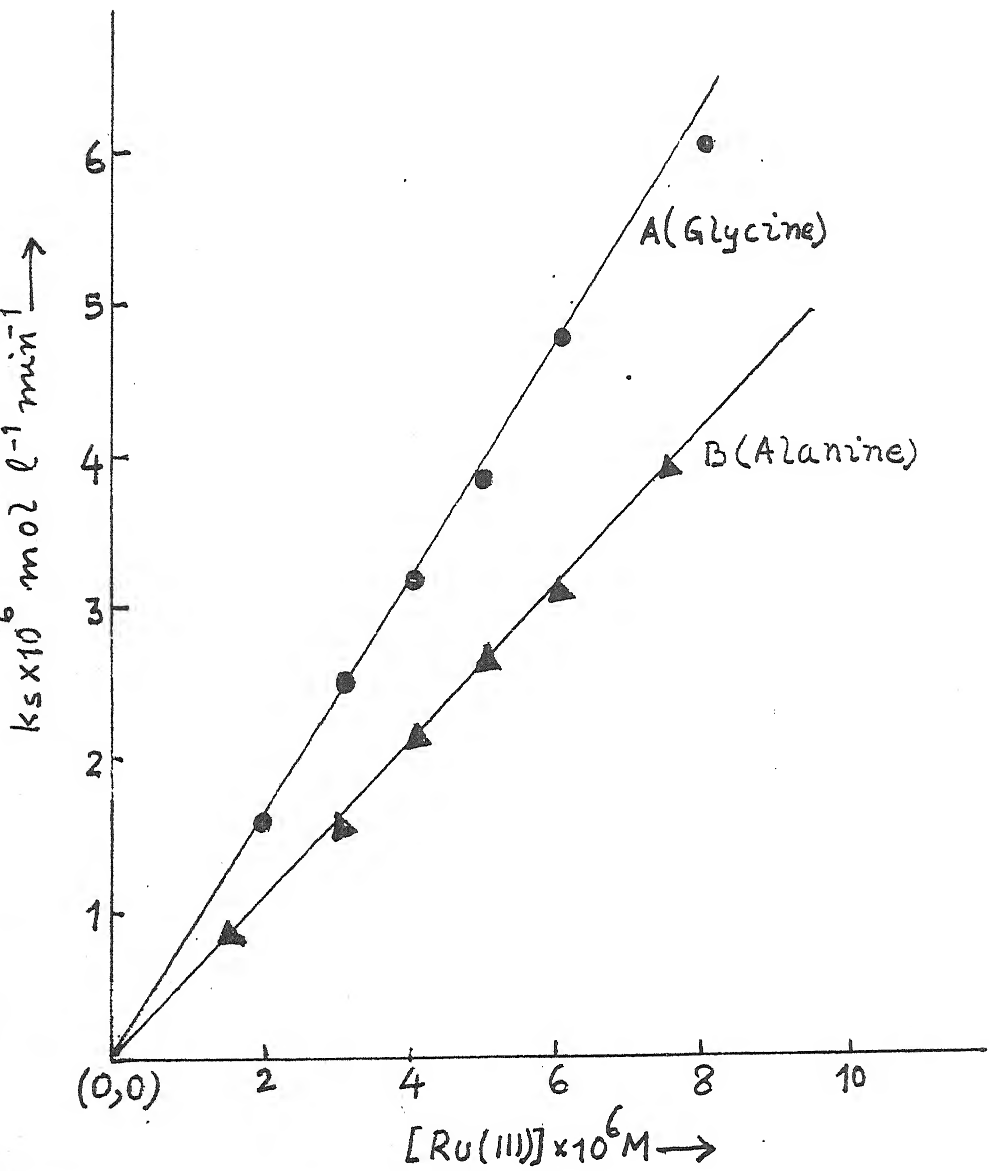

FIG. 5.1: PLOT BETWEEN k_s AND $[Ru(III)]$ AT $30^{\circ}C$

$[CuSO_4] = 1.25(A)$ AND $(1.00(B) \times 10^{-3} M$, $[KCl] = 1.00 \times 10^{-3} M$,
$[Glycine] = 5.00 \times 10^{-2} M$ (A), $[ALANINE] = 5.00 \times 10^{-2} M$ (B),
$[FREE\ BIPYRIDYL] = 5.00 \times 10^{-3} M$, $pH = 10.80$,
$[Na_2CO_3] = 5.00 \times 10^{-2} M$ AND $[NaHCO_3] = 2.00 \times 10^{-3} M$

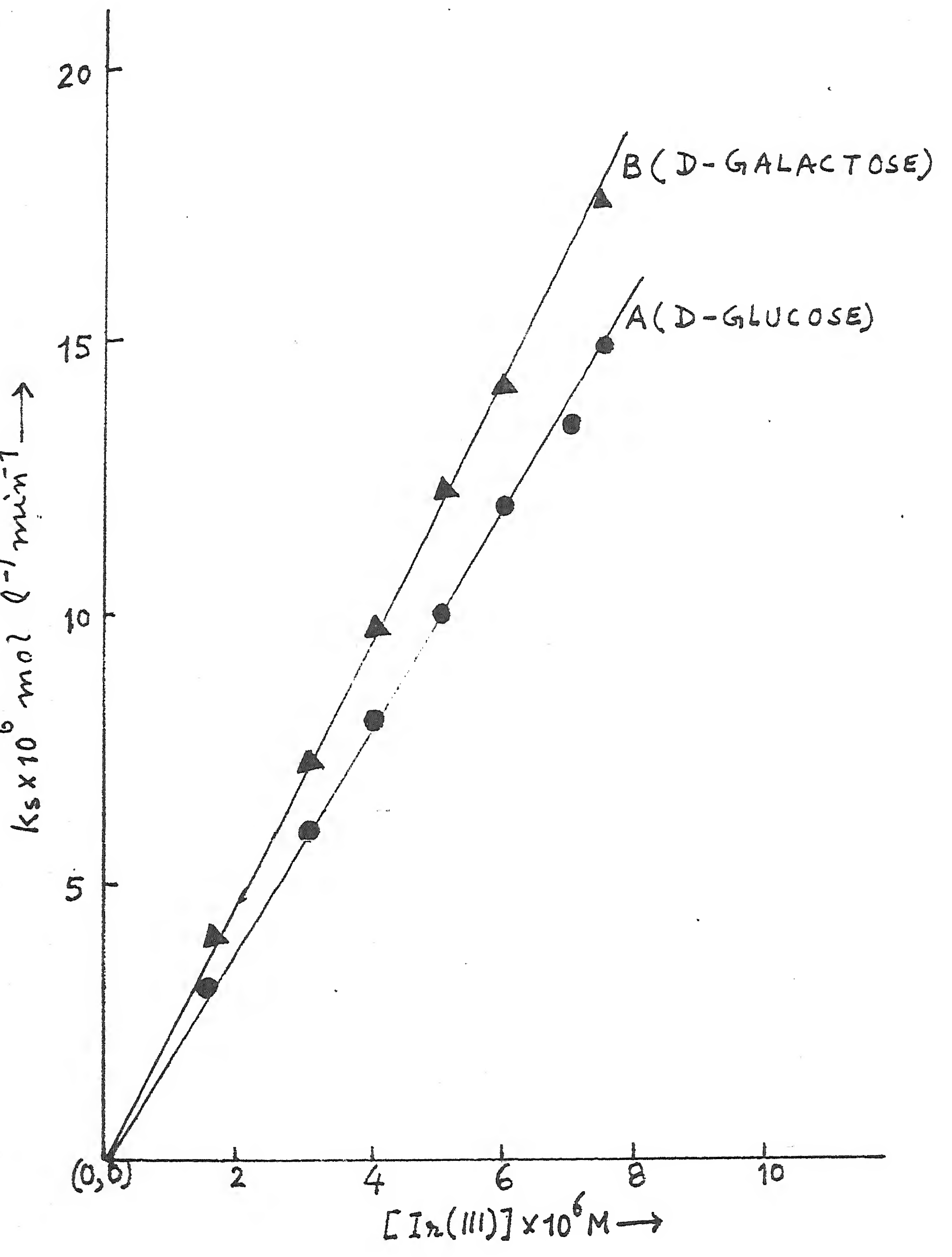

FIG. 5.2: PLOT BETWEEN K_s AND [Ir(III)] AT 30°C
$[CuSO_4] = 1.25 \times 10^{-3}$ N, [SUBSTRATE] $= 5.00 \times 10^{-2}$ M, pH $= 10.80$
[FREE BIPYRIDYL] $= 5.00 \times 10^{-3}$ M, $[KCl] = 2.00 \times 10^{-3}$ M
$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

It is quite evident from the summarised results of tables 5.21 - 5.24 that there is direct proportionality between $[Ru(III)]$ and k_s values in oxidation of glycine and alanine by alkaline copper sulphate, suggesting first-order kinetics with respect to Ru(III). Similarly, k_s values increase in direct proportionality with $[Ir(III)]$ which indicates and confirms first-order dependence on Ir(III) in oxidation of D-glucose and D-galactose.

The above observation regarding dependence of reactions on [Catalyst] is further confirmed on plotting k_s values against $[Ru(III)]$ or $[Ir(III)]$. A straight line passing through origine (Fig. 5.1 and Fig. 5.2) for each case is obtained. The slope value is in agreement fairly with average k_1 values given in tables 5.21 - 5.24 for corresponding reducing agents. This shows first-order kinetics in Ru(III) and Ir(III).

CHAPTER VI

DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO HYDROXYL IONS IN Ru(III) CATALYSED OXIDATION OF GLYCINE AND ALANINE AND Ir(III) CATALYSED OXIDATION OF D-GLUCOSE AND D-GALACTOSE BY ALKALINE COPPER SULPHATE

6 : DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO HYDROXYL IONS IN Ru(III) CATALYSED OXIDATION OF GLYCINE AND ALANINE AND Ir(III) CATALYSED OXIDATION OF D-GLUCOSE AND D-GALACTOSE BY ALKALINE COPPER SULPHATE

In this chapter an attempt has been made to determine the dependence of Ru(III) catalysed oxidation of amino acids and Ir(III) catalysed oxidation of sugars by alkaline copper sulphate on [alkali.] In order to do so, a series of experiments with varying concentrations of sodium bicarbonate at fixed concentrations of all other reactants have been carried out and the results of such experiments have been recorded in tables 6.1 - 6.4, 6.5-6.8, 6.9-6.12 and 6.13 - 6.16 in oxidation of glycine, alanine, D-glucose and D-galactose respectively. When sodium bicarbonate concentration is changed, pH also varies and hence concentration of OH^- is thus varied. All other calculations have been done as in previous chapters.

TABLE 6.1

$[Cu\ SO_4] = 1.25\times10^{-3}M$, $[Glycine] = 5.00\times10^{-2}M$

$[Free\ Bip.] = 5.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 4.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.7 and Temp. $30^{\circ}C$

Time (min)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.25	2.50
25	1.52	2.70
40	1.88	2.40
60	2.40	2.60
90	3.14	2.46
120	3.86	2.40
160	4.86	2.50
200	5.88	2.55
240	6.88	2.50
300	8.38	2.50

Average k_o (excluding *) $= 2.52\times10^{-2}$ ml min^{-1}

$k_o = 2.52\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.2

[Cu SO_4] = 1.25×10^{-3}M, [Glycine] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 8.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.65 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.24	2.20
25	1.48	2.40
40	1.84	2.40
60	2.30	2.30
80	2.74	2.20
120	3.66	2.30
160	4.62	2.40
200	5.58	2.40
240	6.48	2.20
280	7.36	2.20
320	8.28	2.30

Average k_o (excluding *) = 2.30×10^{-2} ml min^{-1}

k_s = 2.30×10^{-6} mol l^{-1} min^{-1}

TABLE 6.3

$[Cu\ SO_4] = 1.25\times10^{-3}M$, $[Glycine] = 5.00\times10^{-2}M$

$[Free\ Bip.] = 5.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$,

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 10.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.60 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
15	1.20	2.00
25	1.42	2.20
40	1.68	1.74
60	2.06	1.90
80	2.48	2.10
120	3.28	2.00
160	4.08	2.00
200	4.88	2.00
250	5.98	2.20
300	7.00	2.04

Average k_0 (excluding *) = 2.01×10^{-2} ml min^{-1}

$k_s = 2.01 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.4

[Cu SO_4] = 1.25×10^{-3}M, [Glycine] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 16.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.45 and Temp. 30°C

Time (min.)	Volume of $K_2 Cr_2 O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_0 = \frac{\triangle x}{\triangle t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.16	1.40
35	1.46	1.50
60	1.82	1.44
100	2.38	1.40
160	3.24	1.43
220	4.08	1.40
300	5.22	1.42
380	6.34	1.40
460	7.46	1.40

Average k_0 (excluding *) = 1.42×10^{-2} ml min^{-1}

$k_0 = 1.42 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.5

[Cu SO_4] = 1.00×10^{-3} M, [Alanine] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ru(III)] = 4.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 4.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.7 and Temp. $30^{\circ}C$

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.16	1.60
25	1.34	1.80
45	1.68	1.70
65	2.02	1.70
100	2.62	1.71
140	3.30	1.71
180	4.00	1.75
220	4.70	1.75
260	5.36	1.65

Average k_0 (excluding *) = 1.71×10^{-2} ml min^{-1}

k_s = 1.71×10^{-6} mol l^{-1} min^{-1}

TABLE 6.6

$[Cu\ SO_4] = 1.00 \times 10^{-3}M$, [Alanine] = $5.00 \times 10^{-2}M$

[Free Bip.] = $5.00 \times 10^{-3}M$, [Ru(III)] = $4.00 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 8.00 \times 10^{-3}M$

[KCl] = $1.00 \times 10^{-3}M$, pH = 10.65 and Temp. 30°C

Time (min)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.18	1.60
25	1.32	1.40
45	1.62	1.50
80	2.16	1.54
120	2.76	1.50
180	3.70	1.56
240	4.60	1.50
300	5.52	1.53
360	6.58	1.60

Average k_o (excluding *) = 1.54×10^{-2} ml min^{-1}

$k_s = 1.54 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.7

[Cu SO_4] = 1.00×10^{-3} M, Alanine = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ru(III)] = 4.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 10.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.60 and Temp. 30°C

Time (min)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\,k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.16	1.40
35	1.43	1.30
60	1.76	1.36
90	2.16	1.33
130	2.70	1.35
180	3.40	1.40
240	4.18	1.30
300	5.00	1.36
360	5.80	1.33
420	6.58	1.30

Average k_0 (excluding *) = 1.38×10^{-2} ml min^{-1}

k_s = 1.38×10^{-6} mol l^{-1} min^{-1}

TABLE 6.8

$[Cu\ SO_4] = 1.00 \times 10^{-3} M$, $[\text{Alanine}] = 5.00 \times 10^{-2} M$

$[\text{Free Bip.}] = 5.00 \times 10^{-3} M$, $[Ru(III)] = 4.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 16.00 \times 10^{-3} M$

$[KCl] = 1.00 \times 10^{-3} M$, pH = 10.45 and Temp. $30^{\circ}C$

Time (min.)	Volume of $K_2 Cr_2 O_7$ (0.50×10^{-3} M) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
15	1.10	1.00
35	1.30	1.00
60	1.54	0.96
100	1.92	0.95
160	2.50	0.96
220	3.10	1.00
280	3.66	0.93
360	4.44	0.97
440	5.20	0.95
520	5.92	0.90

Average k_o (excluding *) $= 0.96 \times 10^{-2}$ ml min^{-1}

$k_s = 0.96 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.9

$[Cu\ SO_4] = 1.25 \times 10^{-3} M$, $[D\text{-glucose}] = 5.00 \times 10^{-2} M$

$[Free\ Bip.] = 5.00 \times 10^{-3} M$, $[I_r(III)] = 5.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 4.00 \times 10^{-3} M$

$[KCl] = 2.00 \times 10^{-3} M$, pH = 10.7 and Temp. 30°C

Time (min)	Volume of $K_2 Cr_2 O_7$ (0.50×10^{-3}N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.78	7.80
25	2.58	8.00
35	3.38	8.00
45	4.16	7.80
60	5.34	7.86
75	6.54	8.00
90	7.72	7.86
105	8.90	7.86
120	10.10	8.00
135	11.30	8.00

Average k_o (excluding *) $= 7.98 \times 10^{-2}$ ml min^{-1}

$k_s = 7.98 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.10

$[Cu\ SO_4] = 1.25x10^{-3}M$, $[D\text{-glucose}] = 5.00x10^{-2}M$

$[Free\ Bip.] = 5.00x10^{-3}M$, $[I_r(III)] = 5.00x10^{-6}M$

$[Na_2CO_3] = 5.00x10^{-2}M$, $[NaHCO_3] = 8.00x10^{-3}M$

$[KCl] = 2.00x10^{-3}M$, pH = 10.65and Temp. 30°C

Time (min)	Volume of $K_2\ Cr_2\ O_7$ ($0.50x10^{-3}$ N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.04	20.80*
15	1.70	7.00
25	2.42	7.20
35	3.12	7.00
45	3.32	7.00
60	4.38	7.06
75	5.34	7.06
90	6.00	7.06
105	7.06	7.06
120	8.14	7.20

Average k_o (excluding *) = $7.07x10^{-2}$ ml min^{-1}

$k_s = 7.07 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.11

[Cu SO_4] = 1.25×10^{-3} M, [D-glucose] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [I_r(III)] = 5.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 10.00×10^{-3} M

[KCl] = 2.00×10^{-3} M, pH = 10.60 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
15	1.64	6.40
25	2.26	6.20
35	2.88	6.20
45	3.52	6.40
60	4.48	6.40
75	5.42	6.26
90	6.36	6.26
105	7.28	6.13
120	8.24	6.40
140	9.54	6.50

Average k_0 (excluding *) = 6.32×10^{-2} ml min^{-1}

k_0 = 6.32×10^{-6} mol l^{-1} min^{-1}

TABLE 6.12

$[Cu\ SO_4] = 1.25 \times 10^{-3} M$, $[\text{D-glucose}] = 5.00 \times 10^{-2} M$

$[\text{Free Bip.}] = 5.00 \times 10^{-3} M$, $[I_r(III)] = 5.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 16.00 \times 10^{-3} M$

$[KCl] = 2.00 \times 10^{-3} M$, pH = 10.45 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_0 = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40 *
15	1.46	4.40
25	1.88	4.20
35	2.32	4.40
45	2.74	4.20
60	3.38	4.26
75	4.02	4.26
90	4.68	4.40
105	5.38	4.66
120	6.06	4.53
135	6.76	4.66
150	7.46	4.66

Average k_0 (excluding *) $= 4.42 \times 10^{-2}$ ml min^{-1}

$k_0 = 4.42 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.13

$[CuSO_4] = 1.25\times10^{-3}M$, [D-galactose] $= 5.00\times10^{-2}M$

[Free Bip.] $= 5.00\times10^{-3}M$, $[I_r(III)] = 5.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 4.00\times10^{-3}M$

$[KCl] = 2.00\times10^{-3}M$, pH = 10.7 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.98	9.60
25	2.92	9.40
35	3.86	9.40
50	5.20	9.33
65	6.62	9.46
80	8.04	9.46
95	9.44	9.33
110	10.86	9.46
125	12.28	9.46

Average k_o (excluding *) $= 9.43\times10^{-2}$ ml min^{-1}

$k_s = 9.43 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.14

[Cu SO_4] = 1.25×10^{-3} M, [D-galactose] = 5.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ir(III)] = 5.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 8.00×10^{-3} M

[KCl] = 2.00×10^{-3} M, pH = 10.65 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.88	8.60
25	2.72	8.40
35	3.58	8.60
45	4.42	8.40
60	5.68	8.40
75	6.88	8.00
90	8.12	8.26
105	9.34	8.13
120	10.62	8.53
135	11.88	8.40

Average k_o (excluding *) = 8.37×10^{-2} ml min^{-1}

k_s = 8.37×10^{-6} mol l^{-1} min^{-1}

TABLE 6.15

$[Cu\ SO_4] = 1.25 \times 10^{-3} M$, $[\text{D-galactose}] = 5.00 \times 10^{-2} M$

$[\text{Free Bip.}] = 5.00 \times 10^{-3} M$, $[I_r(III)] = 5.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 10.00 \times 10^{-3} M$

$[KCl] = 2.00 \times 10^{-3} M$, pH = 10.60 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50 \times 10^{-3} M$) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.78	7.60
25	2.56	7.80
35	3.30	7.40
45	4.06	7.60
60	5.16	7.33
75	6.30	7.60
90	7.48	7.86
105	8.62	7.60
120	9.76	7.60
135	11.52	7.74

Average k_o (excluding *) = 7.61×10^{-2} ml min^{-1}

$k_s = 7.62 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 6.16

$[Cu\ SO_4] = 1.25x10^{-3}M$, [D-galactose] = $5.00x10^{-2}M$

[Free Bip.] = $5.00x10^{-3}M$, $[I_g(III)] = 5.00x10^{-6}M$

$[Na_2CO_3] = 5.00x10^{-2}M$, $[NaHCO_3] = 16.00 \times 10^{-3}M$

[KCl] = $2.00x10^{-3}M$, pH = 10.45 and Temp. 30°C

Time (min.)	Volume of $K_2Cr_2O_7^{=}$ ($0.50x10^{-3}$ N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.56	5.40
25	2.08	5.20
35	2.62	5.40
45	3.16	5.40
60	3.94	5.20
75	4.74	5.33
90	5.56	5.46
105	6.38	5.46
120	7.18	5.33
140	8.24	5.30

Average k_o (excluding *) = 5.35×10^{-2} ml min^{-1}

$k_s = 5.35 \times 10^{-6}$ mol l^{-1} min^{-1}

The kinetic observations recorded in tables 6.1 - 6.4 and 4.2, tables 6.5 - 6.8 & 4.7, tables 6.9 - 6.12 & 3.14 and tables 6.13 - 6.16 & 3.20 have been summarised in tables 6.17, 6.18, 6.19 and 6.20 respectively.

TABLE 6.17

$[Cu\ SO_4] = 1.25 \times 10^{-3}$ M, [Glycine] $= 5.00 \times 10^{-2}$ M,

[Free Bip.] $= 5.00 \times 10^{-3}$ M, [Ru(III)] $= 4.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, [KCl] $= 1.00 \times 10^{-3}$ M

Temp. 30°C

$[NaHCO_3]\ 10^3$ M	pH	$[\bar{OH}] \times 10^4$ M	10^6 ks mol l^{-1} min^{-1}	$10^3 k_1$ min^{-1}
2.00	10.80	6.31	3.20	5.07
4.00	10.70	5.01	2.52	5.03
8.00	10.65	4.46	2.30	5.15
10.00	10.60	3.98	2.01	5.01
16.00	10.45	2.81	1.42	5.05

Average $k_1 = 5.06 \times 10^{-3}$ min^{-1}

TABLE 6.18

[Cu SO_4] = 1.00×10^{-3}M, [Alanine] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [KCl] = 1.00×10^{-3}M

Temp. 30°C

[$NaHCO_3$] x 10^3 M	pH	[OH^-] x 10^4 M	10^6 k_s mol l^{-1} min^{-1}	10^3 k_1 min^{-1}
2.00	10.80	6.31	2.16	3.42
4.00	10.70	5.01	1.71	3.40
6.00	10.65	4.46	1.54	3.45
10.00	10.60	3.98	1.38	3.47
16.00	10.45	2.81	0.96	3.41

Average k_1 = 3.43×10^{-3} min^{-1}

TABLE 6.19

[Cu SO_4] = 1.25×10^{-3}M, [D-glucose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [KCl] = 2.00×10^{-3}M

Temp. 30°C

[$NaHCO_3$] x 10^3 M	pH	[OH^-] x10^4 M	10^6k_s mol l^{-1} min^{-1}	10^3k_1 min^{-1}
2.00	10.80	6.31	10.00	1.58
4.00	10.70	5.01	7.98	1.59
8.00	10.65	4.46	7.07	1.58
10.00	10.60	3.98	6.32	1.56
16.00	10.45	2.81	4.42	1.57

Average k_1 = 1.57×10^{-3} min^{-1}

TABLE 6.20

$[Cu\,SO_4] = 1.25\times10^{-3}M$, $[\text{D-galactose}] = 5.00\times10^{-2}M$

$[\text{Free Bip.}] = 5.00\times10^{-3}M$, $[Ir(III)] = 5.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-3}M$, $[KCl] = 2.00\times10^{-3}M$

Temp. $30^{\circ}C$

$[NaHCO_3]\times10^3$ M	pH	$[OH^-]\times10^4$ M	$10^6 k_s$ mol $l^{-1}min^{-1}$	$10^3 k_1$ min^{-1}
2.00	10.80	6.31	12.22	1.93
4.00	10.70	5.01	9.43	1.88
8.00	10.65	4.46	8.37	1.87
10.00	10.60	3.98	7.61	1.91
16.00	10.45	2.81	5.35	1.91

Average $k_1 = 1.90\times10^{-3}min^{-1}$

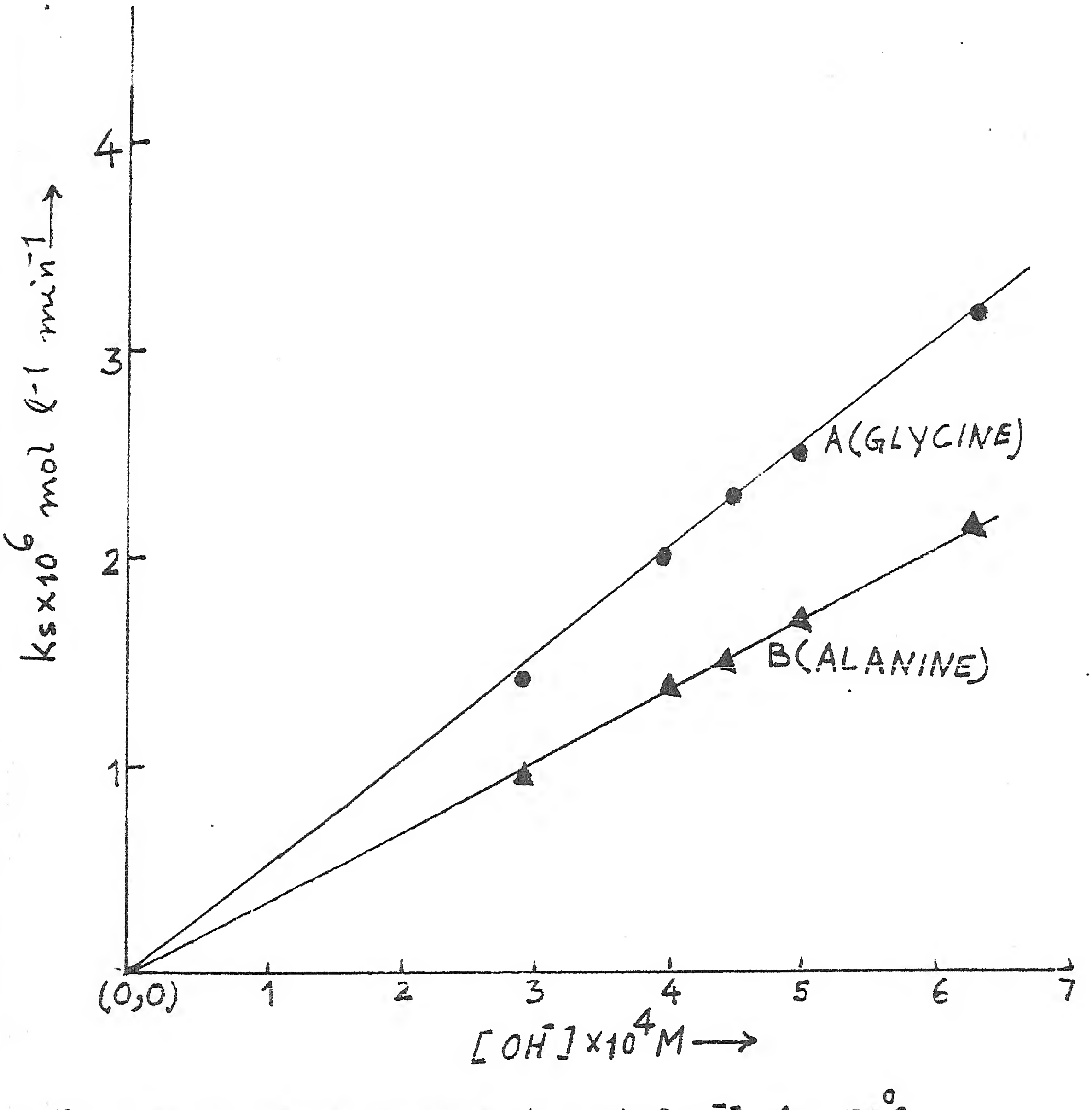

FIG. 6.1: PLOT BETWEEN K_s AND $[OH^-]$ AT 30^0C
$[CuSO_4] = 1{\cdot}25\,(A)$ AND $1{\cdot}00\,(B) \times 10^{-3}$ M ,
$[Ru(III)] = 4{\cdot}00 \times 10^{-6}$ M, $[KCl] = 1{\cdot}00 \times 10^{-3}$ M ,
[FREE BIPYRIDYL] $= 5{\cdot}00 \times 10^{-3}$ M, $[Na_2CO_3] = 5{\cdot}00 \times 10^{-2}$ M,
[GLYCINE] $= 5{\cdot}00 \times 10^{-2}$ M (A) & [ALANINE] $= 5{\cdot}00 \times 10^{-2}$ M (B)

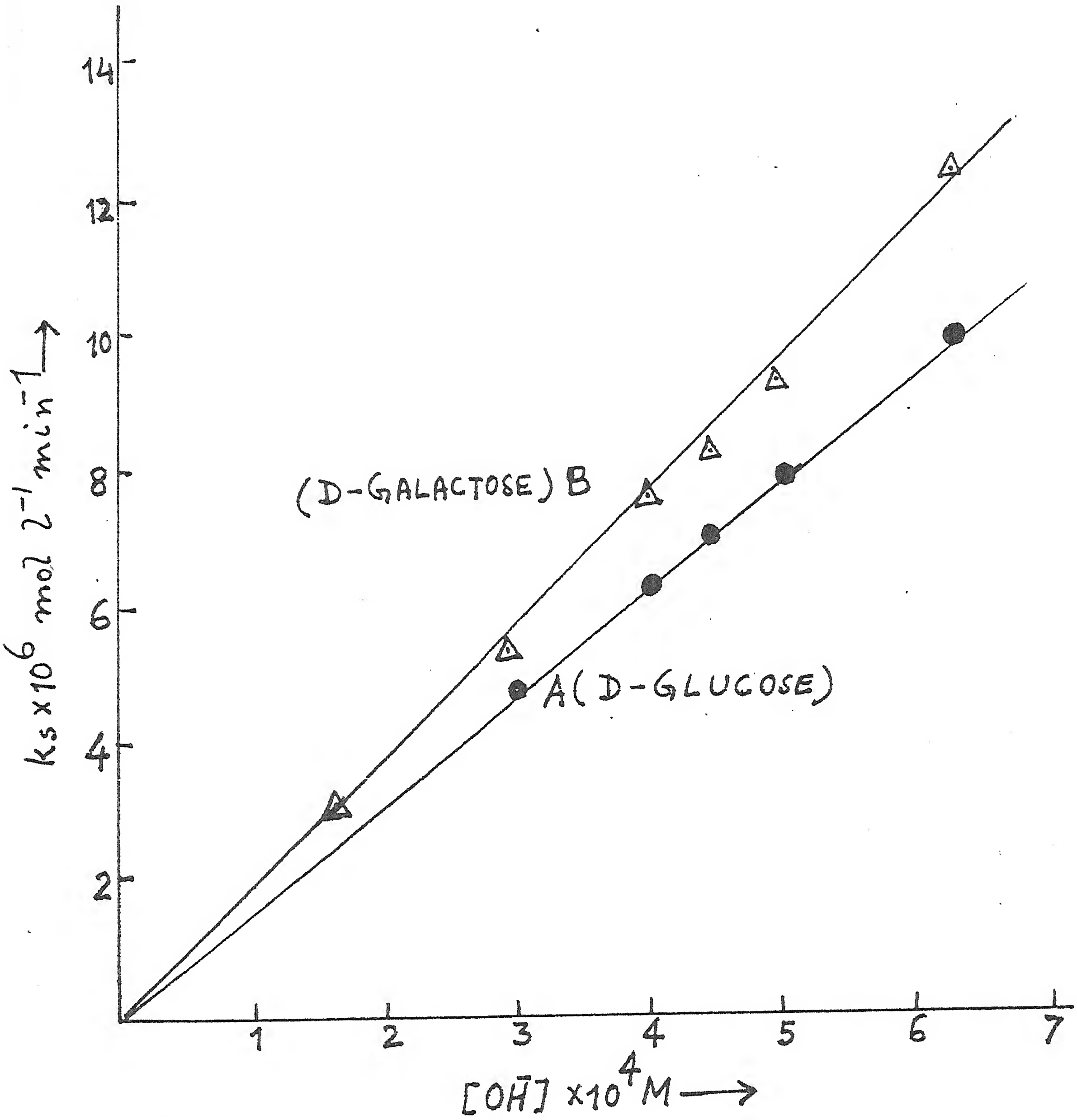

FIG. 6.2: PLOT BETWEEN Ks AND $[OH^-]$ AT 30°C

$[CuSO_4] = 1.25 \times 10^{-3}$ M ; $[Ir(III)] = 5.00 \times 10^{-6}$ M

[FREE BIPYRIDYL] $= 5.00 \times 10^{-3}$ M, $[KCl] = 2.00 \times 10^{-3}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, [SUBSTRATE] $= 5.00 \times 10^{-2}$ M

It is quite clear from the kinetic data of above tables that on increasing the concentration of sodium bicarbonate the value of pH decreases and thus ultimately concentration of OH^- decreases. Thus on decreasing the $[OH^-]$, the value of k_s also decreases showing thus positive effect of hydroxide ion on reaction rate constant. It is also clear that k_s values are in direct proportionality with $[OH^-]$, which proves first order in hydroxyl ions.

This is, further, confirmed by plotting a graph between k_s and $[OH^-]$, which gives a straight line passing through origins (Fig. 6.1) and (Fig. 6.2) whose slope is equal average k_1 value in each case.

On increasing the concentration of sodium bicarbonate the dissociation of sodium carbonate is gradually suppressed. This causes fall in pH and hence decrease in $[OH^-]$ is observed. This explains why $[OH^-]$ is decreased on increasing sodium bicarbonate concentration.

CHAPTER VII

DETERMINATION OF EFFECT OF ADDITION OF POTASSIUM CHLORIDE ON THE RATE OF OXIDATION OF AMINO ACIDS AND SUGARS BY ALKALINE SOLUTION OF COPPER SULPHATE

7 : DETERMINATION OF EFFECT OF ADDITION OF POTASSIUM CHLORIDE ON THE RATE OF OXIDATION OF AMINO ACIDS AND SUGARS BY Cu(II) IN ALKALINE MEDIA

Effect of variation of chloride ions on the rate of oxidation of amino acids viz. glycine and alanine in the presence of alkaline solution of copper sulphate as oxidant and ruthenium(III) chloride as catalyst and on the rate of oxidation of sugars viz. D-glucose and D-galactose catalysed by iridium(III) chloride with copper sulphate as oxidant has been studied by varying the concentration of potassium chloride under the same experimental conditions. The results of such experiments have been recorded in the following tables in the summarized form at constant ionic strength of the medium.

TABLE 7.1

$[Cu\ SO_4] = 1.25 \times 10^{-3}M$, $[Glycine] = 5.00 \times 10^{-2}M$

$[Free\ Bip.] = 5.00 \times 10^{-3}M$, $[Ru(III)] = 4.00 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 2.00 \times 10^{-3}M$

pH = 10.80 and Temp. 30°C

$\mu = 17.50 \times 10^{-2}M$

$[KCl] \times 10^3 M$	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.00	3.20
2.00	2.84
3.00	2.66
4.00	2.12
5.00	1.76
6.00	1.44
7.50	1.02

TABLE 7.2

$[Cu\ SO_4] = 1.00 \times 10^{-3}M$, [Alanine] $= 5.00 \times 10^{-2}M$

[Free Bip.] $= 5.00 \times 10^{-3}M$, $[Ru(III)] = 4.00 \times 10^{-6}M$

$[Na_2CO_3] = 5.00 \times 10^{-2}M$, $[NaHCO_3] = 2.00 \times 10^{-3}M$

pH = 10.80 and Temp. $30^{\circ}C$

$\mu = 17.50 \times 10^{-2}M$

$[KCl] \times 10^3M$	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.00	2.16
2.00	1.82
3.00	1.64
4.00	1.36
5.00	1.00
6.00	0.72
8.00	0.26

TABLE 7.3

$[Cu\ SO_4] = 1.25 \times 10^{-3} M$ $[D\text{-glucose}] = 5.00 \times 10^{-2} M$

$[\text{Free Bip.}] = 5.00 \times 10^{-3} M$, $[I_r(III)] = 5.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 2.00 \times 10^{-3} M$

pH = 10.80 and Temp. 30°C

$\mu = 17.50 \times 10^{-2} M$

$[KCl] \times 10^{3} M$	$k_s \times 10^{6}$ mol l^{-1} min^{-1}
1.00	10.64
2.00	10.00
3.00	9.58
4.00	9.00
5.00	8.52
6.00	7.98
8.00	7.00

TABLE 7.4

$[CuSO_4] = 1.25 \times 10^{-3} M$, $[\text{D-galactose}] = 5.00 \times 10^{-3} M$

$[\text{Free Dip.}] = 5.00 \times 10^{-3} M$, $[Ir(III)] = 5.00 \times 10^{-6} M$

$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 2.00 \times 10^{-3} M$

pH = 10.80 and Temp. 30°C

$\mu = 17.50 \times 10^{-2} M$

$[KCl] \times 10^3$ M	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.00	12.86
2.00	12.22
3.00	11.64
4.00	11.00
5.00	10.46
7.50	10.00
10.00	8.86

It is quite obvious from the kinetic results of tables 7.1 - 7.4 that in oxidation of each amino acid and each sugar under investigation here the value of k_z i.e. zero order rate constant decreases on increasing the concentration of chloride ions which shows that addition of chloride ion has negative effect on the rate of oxidation of reducing amino acids and sugars employed here. This experimental fact has been used while deciding the catalytic species of ruthenium (III) chloride and iridium(III) chloride in the last chapter.

CHAPTER VIII

DETERMINATION OF EFFECT OF VARIATION OF IONIC STRENGTH OF THE MEDIUM ON THE RATE OF OXIDATION OF AMINO ACIDS AND SUGARS BY ALKALINE COPPER SULPHATE

8 : DETERMINATION OF EFFECT OF VARIATION OF IONIC STRENGTH OF THE MEDIUM ON THE RATE OF OXIDATION OF AMINO ACIDS AND SUGARS BY ALKALINE COPPER SULPHATE

In this chapter main aim has been to describe the influence of variation of ionic strength of the medium on reaction velocity constant. The knowledge of effect of variation of iogic strength indicates the type and nature of reactive species involved in the reaction rate determining step. Hence various experiments with varying ionic strengths affected by addition of different amounts of sodium perchlorate have been performed and the results have been summarised in the following tables for oxidation of each substrate.

TABLE 8.1

[Cu SO_4] = 1.25×10^{-3}M, [Glycine] = 10.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8, Temp. 30°C

[$NaClO_4$] x 10^2M	Ionic strength (μ)x10^2 M	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.50	17.50	6.16
3.00	19.00	6.52
5.00	21.00	6.76
10.00	26.00	7.86
20.00	36.00	8.72
30.00	46.00	9.56
40.00	56.00	10.62
50.00	66.00	11.76
60.00	76.00	12.66

TABLE 8.2

$[Cu\ SO_4] = 1.25\times10^{-3}M$, $[Alanine] = 10.00\times10^{-2}M$

$[Free\ Bip.] = 5.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.80 and Temp. 30°C

$[NaClO_4]\times 10^2M$	Ionic Strength (μ)$\times10^2$ M	$k_s\times10^6$ mol l^{-1} min^{-1}
1.50	17.50	4.18
4.00	20.00	4.80
8.00	24.00	5.38
12.00	28.00	6.06
20.00	36.00	7.18
30.00	46.00	8.38
50.00	66.00	10.58
60.00	76.00	11.48

TABLE 8.3

$[Cu\ SO_4] = 1.25x10^{-3}M$, $[\text{D-glucose}] = 5.00x10^{-2}M$

$[\text{Free Bip.}] = 5.00x10^{-3}M$, $[I_r(III)] = 5.00x10^{-4}M$

$[Na_2CO_3] = 5.00x10^{-2}M$, $[NaHCO_3] = 2.00x10^{-3}M$

$[KCl] = 2.00x10^{-3}M$, pH = 10.80 and Temp.

$[NaClO_4] \times 10^2$ M	Ionic strength (μ)$x10^2$ M	$k_s \times 10^6$ mol $l^{-1}min^{-1}$
1.50	17.50	10.04
3.00	19.00	10.54
5.00	21.00	10.88
10.00	26.00	11.38
20.00	36.00	12.46
30.00	46.00	13.52
40.00	56.00	14.36
50.00	66.00	15.68
60.00	76.00	16.98

TABLE 8.4

$[Cu\ SO_4] = 1.25x10^{-3}M$, [D-galactose] $= 5.00x10^{-2}M$

[Free Bip.] $= 5.00x10^{-3}M$, $[I_x(III)] = 5.00x10^{-6}M$

$[Na_2CO_3] = 5.00x10^{-2}M$, $[NaHCO_3] = 2.00x10^{-3}M$

$[KCl] = 2.00x10^{-3}M$, pH = 10.80 and Temp. 30°C

$[NaClO_4] \times 10^2$ M	Ionic strength (μ)x10^2 M	$k_s \times 10^6$ mol l^{-1} min^{-1}
1.50	17.50	12.48
3.00	19.00	12.82
5.00	21.00	13.28
10.00	26.00	13.86
20.00	36.00	14.66
30.00	46.00	15.38
40.00	56.00	16.52
50.00	66.00	17.46
60.00	76.00	18.54

It is clear from the data of tables 8.1 - 8.4 that change in ionic strength has positive effect on the rate of oxidation of amino acids and sugars by alkaline solution of copper sulphate.

CHAPTER IX

DETERMINATION OF EFFECT OF VARIATION OF TEMPERATURE ON VELOCITY CONSTANT OF REACTIONS INVOLVING COPPER SULPHATE AS OXIDANT AND AMINO ACIDS AND SUGARS AS REDUCING SUBSTANCES

9 : DETERMINATION OF EFFECT OF VARIATION OF TEMPERATURE ON VELOCITY CONSTANT OF REACTIONS INVOLVING COPPER SULPHATE AS OXIDANT AND AMINO ACIDS AND SUGARS AS REDUCING SUBSTANCES

Oxidation kinetics of various reactions are generally susciptible to change in temperature and the velocity of reactions increase on increasing the temperature. Keeping this aim in mind, the kinetic results at temperatures 35, 40, and 45^{o}C have been collected as kinetic results at 30^{o}C have already been reported in previous chapters. The results at different temperatures are given in the following tables for oxidation of each amino acid and each sugar employed in the present investigation.

TABLE 9.1

$[Cu\ SO_4] = 1.25x10^{-3}M$, $[Glycine] = 10.00x10^{-2}M$

$[Free\ Bip.] = 5.00x10^{-2}M$, $[Ru(III)] = 4.00x10^{-6}M$

$[KCl] = 1.00x10^{-3}M$, $[Na_2CO_3] = 5.00x10^{-2}M$,

$[NaHCO_3] = 2.00x10^{-3}M$, pH = 10.80, μ = $17.50x10^{-2}M$

Temperature 35°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50x10^{-3}$ M) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.92	9.00
25	2.84	9.20
35	3.72	8.80
45	4.62	9.00
60	6.02	9.33
75	7.38	9.06
90	8.76	9.20
110	10.56	9.00

Average k_o (excluding *) = 9.17×10^{-2} ml/min

$k_s = 9.17x10^{-6}$ mol l^{-1} min^{-1}

TABLE 9.2

$[Cu\ SO_4] = 1.25\times10^{-3}M$, $[Glycine] = 10.00\times10^{-2}M$

$[Free\ Bip.] = 5.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 1.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, $pH = 10.80$, $\mu = 17.50\times10^{-2}M$

Temperature $40^{\circ}C$

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.04	20.80*
10	1.74	14.00
15	2.42	13.60
20	3.08	13.20
30	4.38	13.00
40	5.74	13.60
50	7.10	13.60
60	8.44	13.40
70	9.80	13.60
80	11.14	13.40

Average k_o (excluding *) = 13.49×10^{-2} ml/min

$k_s = 13.49 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 9.3

$[CuSO_4] = 1.25\times10^{-3}M$, $[Glycine] = 10.00\times10^{-2}M$

$[Free\ Bip.] = 5.00\times10^{-3}M$, $[Ru(III)] = 4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.80, $\mu = 17.50\times10^{-2}M$

Temperature 45°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
10	1.94	18.40
15	2.94	20.00
20	3.90	19.20
25	4.84	18.80
30	5.80	19.20
40	7.76	19.60
50	9.70	19.40
60	11.66	19.60

Average k_o (excluding *) = 19.28×10^{-2} ml/min

$k_s = 19.28\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 9.4

$[Cu\ SO_4] = 1.25\times10^{-3}M$, [Alanine] = $10.00\times10^{-2}M$

[Free Bip.] = $5.00\times10^{-3}M$, [Ru(III)] = $4.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH = 10.80, $\mu = 17.50\times10^{-2}M$

Temperature 35°C

Time (min.)	Volume of $K_2\ Cr_2\ O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ m l/min
0	0.00	--
5	1.02	20.40*
15	1.60	5.80
25	2.16	5.60
35	2.76	6.00
50	3.64	5.86
65	4.50	5.73
80	5.40	6.00
100	6.56	5.80
120	7.74	5.90
140	8.90	5.80

Average k_o (excluding *) = 5.83×10^{-2} ml min^{-1}

$k_s = 5.83 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 9.5

[Cu SO_4] = 1.25×10^{-3} M, [Alanine] = 10.00×10^{-2} M

[Free Bip.] = 5.00×10^{-3} M, [Ru(III)] = 4.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 1.00×10^{-3} M, pH = 10.80, μ = 17.50×10^{-2} M

Temperature 40°C

Time (min.)	Volume of $K_2 Cr_2 O_7$ (0.50×10^{-3} N) in ml	10^2 k_o = $\frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
15	1.90	8.80
25	2.80	9.00
35	3.66	8.60
45	4.54	8.80
55	5.42	8.80
65	6.32	9.00
75	7.24	9.20
90	8.58	8.93
105	9.94	9.06

Average k_o (excluding *) = 8.91×10^{-2} ml/min^{-1}

k_s = 8.91×10^{-6} mol l^{-1} min^{-1}

TABLE 9.6

[Cu SO_4] = 1.25×10^{-3}M, [Alanine] = 10.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-2}M, pH = 10.80, μ = 17.50×10^{-2}M

Temperature 45°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.02	20.40*
10	1.74	14.40
20	3.16	13.60
30	4.50	13.40
40	5.86	13.60
50	7.18	13.20
60	8.50	13.20
70	9.86	13.60
80	11.20	13.40

Average k_o (excluding *) = 13.55×10^{-2} ml/min

k_s = 13.55×10^{-6} mol l^{-1} min^{-1}

TABLE 9.7

$[Cu\ SO_4] = 1.25\times10^{-3}M$, $[\text{D-glucose}] = 5.00\times10^{-2}M$

$[\text{Free Bip}] = 5.00\times10^{-3}M$, $[K_F(III)] = 5.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 2.00\times10^{-3}M$, pH $= 10.80$, $\mu = 17.50\times10^{-2}M$

Temperature 35°C

Time (min.)	Volume of $K_2\,Cr_2\,O_7$ $(0.50\times10^{-3}N)$ in ml	$10^2\ k_o = \dfrac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
10	1.80	16.00
15	2.56	15.20
20	3.34	15.60
25	4.14	16.00
30	4.90	15.60
40	6.44	15.40
50	8.04	16.00
60	9.62	15.80

Average k_o (excluding *) $= 15.70\times10^{-2}$ ml/min

$k_s = 15.70\times10^{-6}$ mol^{-1} min^{-1}

TABLE 9.3

[Cu SO_4] = 1.25×10^{-3}M, [D-glucose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ir(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.80, μ = 17.50×10^{-2}M

Temperature 40°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3}N) in ml	$10^2\,k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	– –
5	1.02	20.40*
10	2.20	24.00
15	3.44	24.80
20	4.66	24.40
25	5.88	24.40
30	7.08	24.00
35	8.28	24.00
40	9.50	24.40
45	10.74	24.80

Average k_o (excluding *) = 24.35×10^{-2} ml min^{-1}

k_s = 24.35×10^{-6} mol l^{-1} min^{-1}

TABLE 9.9

$[Cu\,SO_4] = 1.25 \times 10^{-3}$ M, $[\text{D-glucose}] = 5.00 \times 10^{-2}$ M

$[\text{Free Bip.}] = 5.00 \times 10^{-3}$ M, $[I_r(III)] = 5.00 \times 10^{-6}$ M

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M

$[KCl] = 2.00 \times 10^{-3}$ M, pH $= 10.80$, $\mu = 17.50 \times 10^{-2}$ M

Temperature 45°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} M) in ml	$10^2 k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.00	20.00*
10	2.68	33.60
15	4.38	34.00
20	6.04	33.20
25	7.68	32.80
30	9.36	33.60
35	11.00	32.80
38	12.02	34.00

Average k_o (excluding *) $= 33.40 \times 10^{-2}$ ml/min

$k_s = 33.40 \times 10^{-6}$ mol l^{-1} min^{-1}

TABLE 9.10

$[Cu\ SO_4] = 1.25\times10^{-3}$ M, $[\text{D-galactose}] = 5.00\times10^{-2}$ M

$[\text{Free Bip.}] = 5.00\times10^{-3}$ M, $[Ir(III)] = 1.50\times10^{-6}$ M

$[Na_2CO_3] = 5.00\times10^{-2}$ M, $[NaHCO_3] = 2.00\times10^{-3}$ M

$[KCl] = 2.00\times10^{-3}$ M, pH = 10.80, $\mu = 17.50\times10^{-2}$ M

Temperature 35°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.56	5.40
25	2.12	5.60
35	2.70	5.80
45	3.26	5.60
65	4.38	5.60
85	5.52	5.70
110	6.92	5.60
140	8.54	5.40

Average k_o (excluding *) $= 5.59\times10^{-2}$ ml/min

$k_s = 5.59\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 8.11

$[CuSO_4] = 1.25\times10^{-3}M$, $[\text{D-galactose}] = 5.00\times10^{-2}M$

$[\text{Free Bip.}] = 5.00\times10^{-3}M$, $[Ir(III)] = 1.50\times10^{-6}M$

$[KCl] = 2.00\times10^{-3}M$, $[Na_2CO_3] = 5.00\times10^{-2}M$

$[NaHCO_3] = 2.00\times10^{-3}M$, pH = 10.80, $\mu = 17.50\times10^{-2}M$

Temperature 40°C

Time (min.)	Volume of $K_2Cr_2O_7$ ($0.50\times10^{-3}N$) in ml	$10^2\,k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	--
5	1.02	20.40*
15	1.92	9.00
25	2.84	9.20
35	3.72	8.80
45	4.62	9.00
60	6.62	9.33
75	7.38	9.06
90	8.76	9.20
110	10.56	9.00
130	12.32	8.80

Average k_o (excluding *) = 9.04×10^{-2} ml/min

$k_s = 9.04\times10^{-6}$ mol l^{-1} min^{-1}

TABLE 9.12

[Cu SO_4] = 1.25×10^{-3}M, [D-galactose] = 5.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 1.50×10^{-6}M

[KCl] = 2.00×10^{-3}M, [Na_2CO_3] = 5.00×10^{-2}M

[$NaHCO_3$] = 2.00×10^{-3}M, pH = 10.8, μ = 17.50×10^{-2}M

Temperature 45°C

Time (min.)	Volume of $K_2Cr_2O_7$ (0.50×10^{-3} N) in ml	$10^2\ k_o = \frac{\Delta x}{\Delta t}$ ml/min
0	0.00	- -
5	1.00	20.00*
10	1.80	16.00
15	2.62	16.40
20	3.40	15.60
25	4.20	16.00
40	6.68	16.53
55	9.08	16.00
70	11.50	16.13

Average k_o (excluding *) = 16.09×10^{-2} ml/min

k_s = 16.09×10^{-6} mol l^{-1} min^{-1}

The results of tables 9.1 - 9.3 and table 3.2, tables 9.4 - 9.6 & table 3.8, tables 9.7 - 9.9 & table 3.14 and tables 9.10 - 9.12 & table 3.16 have been summarised in tables 9.13, 9.14, 9.15 and 9.16 respectively.

TABLE 9.13

$[Cu\ SO_4] = 1.25\times10^{-3}M$, $[Glycine] = 10.00\times10^{-2}M$

$[Free\ Bip.] = 5.00\times10^{-3}M$, $[Ru(III)] = 5.00\times10^{-6}M$

$[Na_2CO_3] = 5.00\times10^{-2}M$, $[NaHCO_3] = 2.00\times10^{-3}M$

$[KCl] = 1.00\times10^{-3}M$, pH $= 10.8$ and $\mu = 17.50\times10^{-2}M$

Temperature °C	$k_s \times 10^6$ mol l^{-1} min^{-1}
30	6.19
35	9.17
40	13.49
45	19.28

TABLE 9.14

[Cu SO_4] = 1.25×10^{-3}M, [Alanine] = 10.00×10^{-2}M

[Free Bip.] = 5.00×10^{-3}M, [Ru(III)] = 4.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 1.00×10^{-3}M, pH = 10.8 and

μ = 17.50×10^{-2}M

Temperature °C	$k_s \times 10^6$ mol l^{-1} min^{-1}
30	4.17
35	5.83
40	8.91
45	13.55

TABLE 9.15

[Cu SO_4] = 1.25×10^{-3}M, [D-glucose] = 5.00×10^{-3}M

[Free Bip.] = 5.00×10^{-3}M, [I_r(III)] = 5.00×10^{-6}M

[Na_2CO_3] = 5.00×10^{-2}M, [$NaHCO_3$] = 2.00×10^{-3}M

[KCl] = 2.00×10^{-3}M, pH = 10.80 and

μ = 17.50×10^{-2}M

Temperature °C	$k_s \times 10^6$ mol l^{-1} min^{-1}
30	10.00
35	15.70
40	24.35
45	33.40

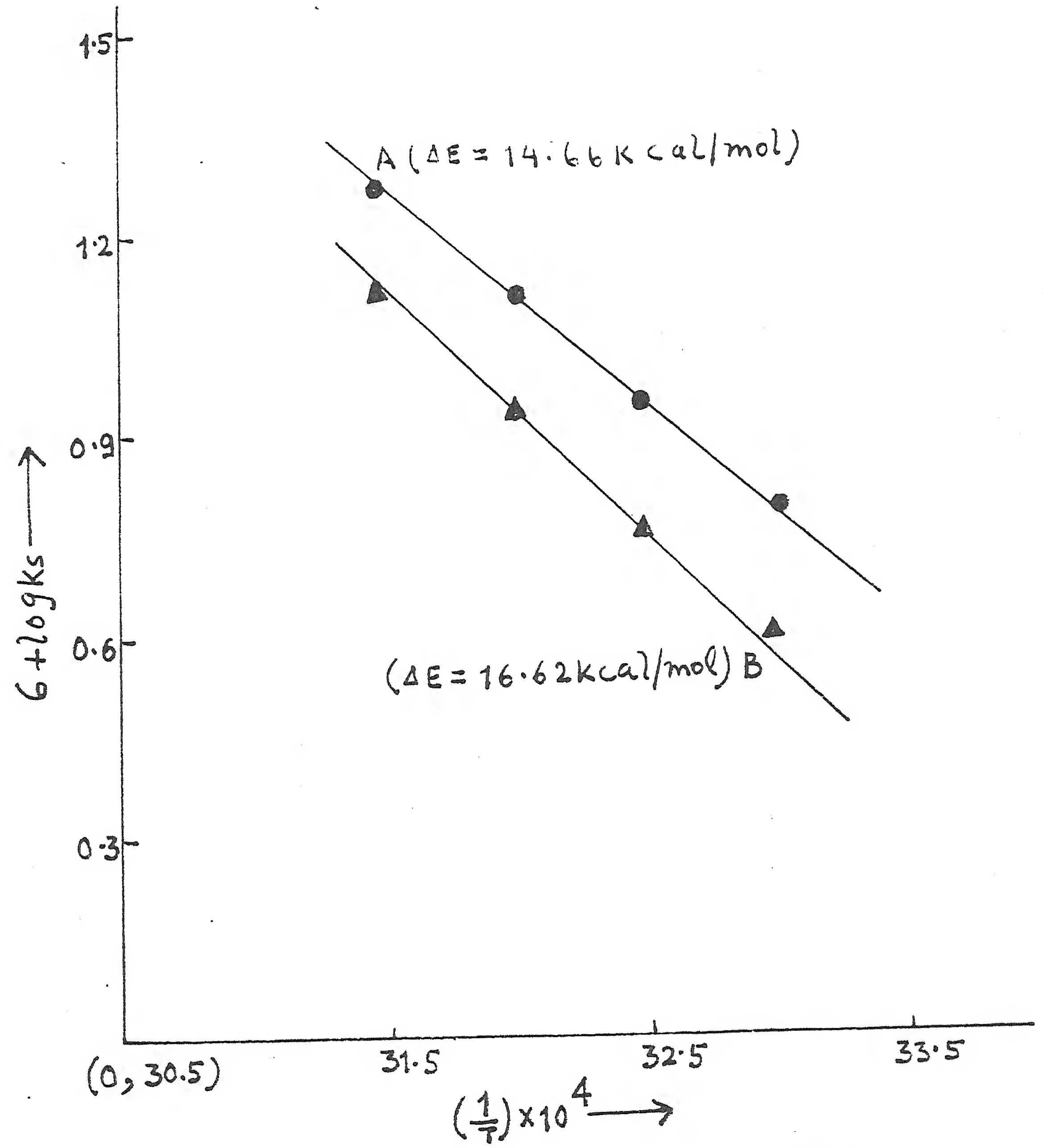

FIG. 9.1: PLOT BETWEEN log ks AND (1/T)

$[CuSO_4] = 1.25 \times 10^{-3}$ N, [GLYCINE] $= 10.00 \times 10^{-2}$ (A) M, $[Ru(III)] = 5.00 \times 10^{-6}$ M (A)

[ALANINE] $= 10.00 \times 10^{-2}$ (B) M, $[Ru(III)] = 4.00 \times 10^{-6}$ M (B), pH $= 10.80$

$[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $[NaHCO_3] = 2.00 \times 10^{-3}$ M, $[KCl] = 1.00 \times 10^{-3}$ M

[Free BIPYRIDYL] $= 5.00 \times 10^{-3}$ M, $\mu = 17.50 \times 10^{-2}$ M

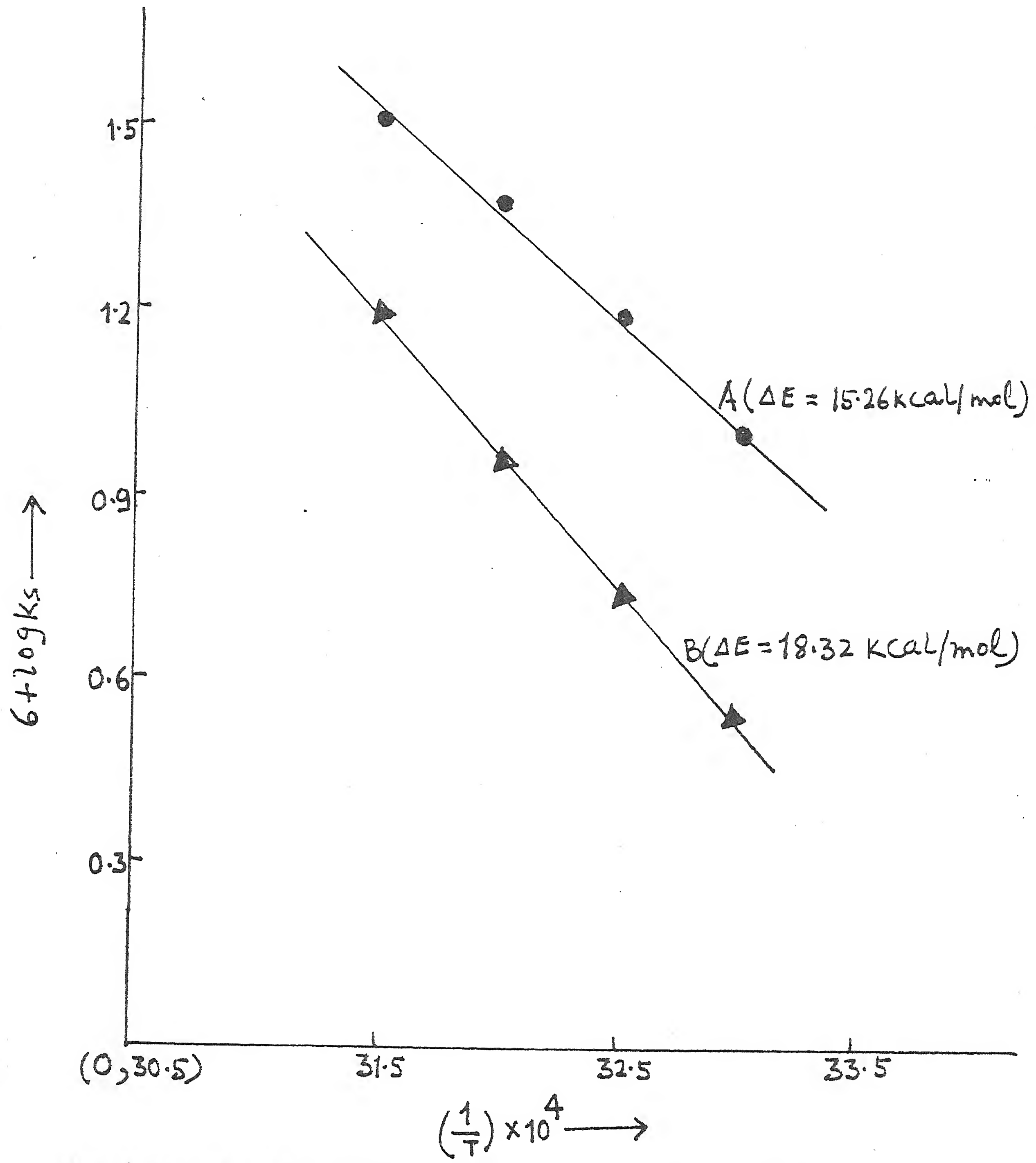

FIG.9.2: PLOT BETWEEN logks AND (1/T)

$[CuSO_4] = 1.25 \times 10^{-3} N$, $[SUBSTRATE] = 5.00 \times 10^{-3}$ (A → D-GLUCOSE AND B → D-GALACTOSE), $[Ir(III)] = 5.00 \times 10^{-6} M$, $\mu = 17.50 \times 10^{-2} M$
$[Na_2CO_3] = 5.00 \times 10^{-2} M$, $[NaHCO_3] = 2.00 \times 10^{-3} M$, $p^H = 10.80$
[FREE BIPYRIDYL] $= 5.00 \times 10^{-3} M$, $[KCl] = 2.00 \times 10^{-3} M$

TABLE 9.16

[Cu SO_4] = 1.25×10^{-3} M, [D-galactose] = 5.00×10^{-3} M

[Free Bip.] = 5.00×10^{-3} M, [I_r(III)] = 5.00×10^{-6} M

[Na_2CO_3] = 5.00×10^{-2} M, [$NaHCO_3$] = 2.00×10^{-3} M

[KCl] = 2.00×10^{-3} M, pH = 10.80 and μ = 17.50×10^{-2} M

Temperature °C	$k_s \times 10^6$ mol ^{1} l^{-1} min^{-1}
30	3.60
35	5.59
40	9.04
45	16.09

The results of tables 9.13, 9.14, 9.15 and table 9.16 have been reproduced graphically. A straight line is obtained on plotting log k_s against (1/T). The slope of the line gives the value equal to − ΔE/2.03R. Thus from the slope (Fig. 9.1A, 9.1B, 9.2A and 9.2B) the value of ΔE i.e. energy of activation is calculated. The value of ΔE for the oxidation of glycine, alanine, D-glucose and D-galactose was found to be 14.66, 16.62, 15.26 and 18.32 K cal/mol, respectively.

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CHAPTER X

DISCUSSION AND INTERPRETATION OF EXPERIMENTAL RESULTS

10 : This chapter contains the summarised results obtained in the studies of oxidation kinetics involving copper sulphate as oxidant in the presence of 2,2' - bipyridyl and amino acids viz. glycine and alanine and sugars viz. D-glucose and D-galactose as reducing materials in the presence of Na_2CO_3 and $NaHCO_3$ buffer solution using Ru(III) chloride and iridium(III) chloride as homogeneous catalyst in oxidation of amino acids and sugars, respectively. These summarised data have been, further, analytically interpreted to elucidate the reaction schemes for the oxidation of amino acids and sugars. The rate law has been, thereafter, derived on the basis of proposed reaction steps. In the following section summarised results have been noted in oxidation of glycine, alanine, D-glucose and D-galactose by copper sulphate.

10.1 : SUMMARY OF KINETIC RESULTS

The following kinetic observations have been noted in Ru(III) catalysed oxidation of glycine and alanine and Ir(III) catalysed oxidation of D-glucose and D-galactose by alkaline solution of copper sulphate.

(1) All the reactions have been found to follow zero-order kinetics in copper sulphate.

(2) The order of the reaction with respect to all substrates i.e. glycine, alanine, D-glucose and D-galactose is one.

(3) First order dependence on hydroxide concentration in all cases has been observed.

(4) In oxidation of glycine and alanine first - order kinetics with respect to ruthenium(III) chloride has been observed. In oxidation of D-glucose and D-galactose also first-order dependence on iridium(III) chloride concentration has been observed.

(5) Successive addition of potassium chloride in oxidation of all the substrates decreased their oxidation rates, showing thus decreasing

effect of chloride ions on oxidation of all the substrates.

(6) Ionic strength variation indicated positive effect on the reaction rate.

(7) Increase in temperature increased the velocity constant in all cases significantly showing thus marked effect of temperature variation.

10.2 : REACTIVE SPECIES OF RUTHENIUM(III) CHLORIDE IN OXIDATION OF AMINO ACIDS BY ALKALINE COPPER SULPHATE

It has been observed experimentally that on increasing the concentration of potassium chloride the value of rate constant decreases in oxidation of both amino acids i.e. glycine and alanine by alkaline solution of copper sulphate. The decreasing effect of added chloride ions on reaction rate suggests that the following equilibrium exists, and the equilibrium mentioned here has tendency to shift

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5H_2O]^{2-} + Cl^- \quad \text{---(1)}$$

to right direction. Thus either $[RuCl_6]^{3-}$ or $[RuCl_5H_2O]^{2-}$ may be taken as catalytic species. When $[RuCl_6]^{3-}$ is taken as reactive species, the rate law requires positive effect of chloride ions contrary to the observed negative effect Hence it cannot be taken as reactive species $[RuCl_5.H_2O]^{2-}$ when assumed a reactive species, it shows negative effect of chloride ions and hence $[RuCl_5\ H_2O]^{2-}$ is the real catalytic species of ruthenium(III) chloride[1,2].

10.3 : REACTIVE SPECIES OF IRIDIUM(III) CHLORIDE IN OXIDATION OF SUGARS BY ALKALINE SOLUTION OF COPPER SULPHATE

Studies of oxidation of sugars viz D-glucose and D-galactose by alkaline copper sulphate catalysed by iridium(III) chloride in the presence of various amounts of potassium chloride shows that on increasingh chloride ions the rate constant decreases. Thus decreasing effect of chloride ions suggests the following equilibrium(1) to exist which has tendency to move to right direction[3].

$$[IrCl_6]^{3-} + H_2O \rightleftharpoons [IrCl_5H_2O]^{2-} + Cl^- \quad ---(1)$$

Thus association property of chloride ions with $[IrCl_5H_2O]^{2-}$ is remote. This indicates that $[IrCl_6]^{3-}$ cannot be assumed to be reaction species iridium(III) chloride because when rate law is derived on its basis, the rate law requires positive effect of chloride ions contrary to the observed negative effect of chloride ions on the reaction rate Hence the next choice is $[IrCl_5 H_2O]^{2-}$ which, when taken as reactive species, gives rate law capable of explaining negative effect of chloride

ions on rate. Hence $[IrCl_5 H_2O]^{2-}$ is the real catalytic species. Although earlier workers have also reported some different reactive species of iridium(III) chloride but those species are not conforming to the observed kinetics data here.

10.4 : MECHANISM OF OXIDATION OF AMINO ACIDS BY ALKALINE COPPER SULPHATE CATALYSED BY Ru(III) CHLORIDE

The following reaction steps are suggested for the title reactions on the basis of kinetic investigations carried out in previous chapters. Zero-order dependence on copper sulphate suggests that Cu(II) is involved in a fast step after slow and rate determining step.

$$AA + OH^- \overset{K_1}{\rightleftharpoons} AA^- + H_2O \quad \text{--- (i)}$$

$$\underset{(C_1)}{[RuCl_6]^{3-}} + H_2O \overset{K_2}{\rightleftharpoons} \underset{(C_2)}{[RuCl_5H_2O]^{2-}} + Cl^- \quad \text{--- (ii)}$$

$$\underset{(C_2)}{[RuCl_5H_2O]^{2-}} + AA^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{(C_3)}{[RuCl_5.AA^-]^{3-}} + H_2O \quad \text{--- (iii)}$$

where forward reaction of step (3) is slow and rate determining step.

$$C_3 + Cu(II)^* + H_2O \longrightarrow Cu(I)^* + \text{Products} + [RuCl_5H_2O]^{2-} \quad \text{--- (iv)}$$

where AA is amino acid and AA^- is its anion.

$[Cu(II)^*] = [Cu(Bip)_2]^{2+}$ and $[Cu(I)^*] = [Cu(Bip)_2^+]$

Now the rate of the reaction can be expressed in terms of rate of loss of $[Cu(II)]^{*}$ with the help of above reaction steps as given by expression (1)

$$\frac{-d\,[Cu(II)^{*}]}{dt} = k_3\,[C_2]\,[AA^{-}] \qquad \ldots (1)$$

The total concentration of ruthenium(III) chloride i.e. $[Ru(III)]_T$ may be written as eqn (2).

$$[Ru(III)]_T = [C_1] + [C_2] + [C_3] \qquad \ldots (2)$$

From step (ii) we have

$$K_2 = \frac{[C_2]\,[Cl^{-}]}{[C_1][H_2O]}$$

$$\text{or} \quad [C_1] = \frac{[C_2][Cl^{-}]}{K_2\,[H_2O]}$$

$$\text{or} \quad [C_1] = \frac{[C_2][Cl^{-}]}{K_2'} \qquad \ldots (3)$$

From step (III) we have

$$K_3 = \frac{[C_3]\,[H_2O]}{[C_2]\,[AA^{-}]}$$

$$\text{or} \quad [C_3] = \frac{K_3\,[C_2][AA^{-}]}{[H_2O]}$$

$$\text{or} \quad [C_3] = K_3'\,[C_2]\,[AA^{-}] \qquad \ldots (4)$$

where $K_3 = k_3/k_{-3}$ and

$$K_3' = K_3/[H_2O]$$

On substituting the value of $[C_1]$ and $[C_3]$ from eqns (3) and (4) respectively in eqn (2) we have eqn (5)

$$[Ru(III)]_T = \frac{[C_2][Cl^-]}{K_2'} + [C_2] + K_3' [C_2][AA^-]$$

or $K_2' [Ru(III)]_T = [C_2] [Cl^-] + K_2' + K_2' K_3' [AA^-]$

$$\text{or } [C_2] = \frac{K_2' [Ru(III)]_T}{[Cl^-] + K_2' + K_2' K_3' [AA^-]}$$

$$\text{or } [C_2] = \frac{K_2' [Ru(III)]_T}{[Cl^-] + K_2' (1 + K_3' [AA^-])} \quad \ldots (5)$$

By comparing eqns (1) and (5) we have

$$-\frac{d [Cu(II)^*]}{dt} = \frac{k_3 K_2' [Ru(III)]_T [AA^-]}{[Cl^-] + K_2' (1+ K_3' [AA^-])} \quad \ldots (6)$$

From step (1) we have

$$K_1 = \frac{[A A^-][H_2O]}{[AA] [OH^-]}$$

$$\text{or} \quad [AA^{-}] = \frac{K_1 [AA][OH^{-}]}{[H_2O]}$$

$$\text{or} \quad [AA^{-}] = K_1' [AA][OH^{-}] \qquad \ldots (7)$$

$$\text{where} \quad K_1' = K_1/[H_2O]$$

On substituting $[AA^{-}]$ value from eqn (7) in eqn(6) we have

$$\frac{-d\, Cu(III)^{*}}{dt} = \frac{k_3\, K_2'\, K_1' [Ru(III)]_T [AA] [OH^{-}]}{[Cl^{-}] + K_2' (1 + K_1' K_3' [AA][OH^{-}])} \qquad \ldots (8)$$

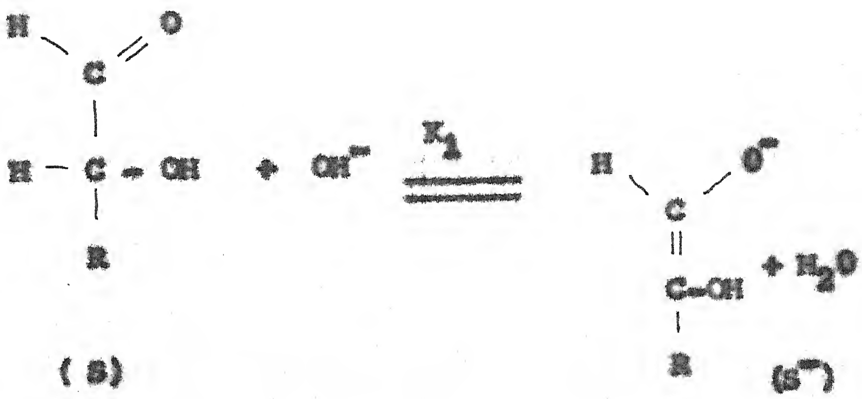
Further on assuming $1 \gg K_3' K_1'$ AA OH^{-} the eqn(8) may be written as eqn (9) in the light of above assumption

$$\frac{-d\,[Cu(II)]^{*}}{dt} = \frac{k_3\, K_1'\, K_2' [Ru(III)]_T [AA] [OH^{-}]}{[Cl^{-}] + K_2'} \qquad \ldots (9)$$

The rate law (9) fully explains all the observed kinetics in oxidation of glycine and alanine by alkaline copper sulphate.

10.3 : MECHANISM OF OXIDATION OF SUGARS BY ALKALINE COPPER SULPHATE CATALYSED BY IRIDIUM(III) CHLORIDE

Considering the summarised kinetic results given in section 10.1 the following reaction path is suggested for the oxidation of sugars viz. D-glucose and D-galactose by alkaline copper sulphate. It is well known that, in the presence of alkali, reducing sugars undergo a tautomeric change through the formation of an intermediate enediol anion. Since in the present case reaction rate is directly proportional to the $[OH^-]$ hence it is the enediol anion which after interaction with iridium(III) chloride species forms an intermediate which is being fast oxidised by $[Cu(Bip)_2^{2+}]$ giving the final product and soluble $[Cu(Bip)_2^{+}]$. Hence the reaction scheme is given as following steps.



... (1)

(S) (S^-)

$$[Ir(Cl_6)]^{3-} + H_2O \xrightleftharpoons{K_2} [Ir\,Cl_5\,H_2O]^{2-} + Cl^- \quad \ldots \text{(ii)}$$

$(C_1) \qquad\qquad (C_2)$

$$\bar{S} + C_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [IrCl_5.\bar{S}]^{3-} + H_2O \quad \ldots \text{(iii)}$$

(C_3)

$$C_3 + [Cu\,(Bip)_2]^{2+} + H_2O \xrightarrow[\text{fast}]{k_4} [RuCl_5H_2O]^{2-} + [Cu\,(Bip)_2]^{+}$$

$$+ \text{Product} \quad .. \text{(iv)}$$

where forward reaction of step (iii) is slow step.

The rate of the reaction can be written in terms of rate of loss of $[Cu(II)]^*$ by eqn (1) where $[Cu(II)]^* = [Cu(Bip)_2]^{2+}$

$$-\frac{d\,[Cu(II)^*]}{dt} = k_3\,[\bar{S}]\,[C_2] \quad \ldots \quad (1)$$

The total concentration of iridium(III) chloride i.e. $[Ir(III)]_T$ may be written as

$$[Ir(III)]_T = [C_1] + [C_2] + [C_3] \quad \ldots \quad (2)$$

Now from step (ii) we have

$$K_2 = \frac{[C_2][Cl^-]}{[C_1][H_2O]}$$

$$\text{or } [C_1] = \frac{[C_2]\,[Cl^-]}{K_2\,[H_2O]}$$

$$\text{or } [C_1] = \frac{[C_2]\,[Cl^-]}{K_2'} \qquad \dots (3)$$

Also from step (iii)

$$K_3 = \frac{[C_3]\,[H_2O]}{[S^-]\,[C_2]}$$

$$\text{or } K_3 = \frac{K_3}{[H_2O]} \quad [S^-]\,[C_2]$$

$$\text{or } [C_3] = K_3'\,[\bar{S}]\,[C_2] \qquad \dots (4)$$

On substituting the value of $[C_1]$ and $[C_3]$ from eqns (3) and (4) respectively in eqn (2) we have eqn(5).

$$[I_r\,(III)]_T = \frac{[C_2][Cl^-]}{K_2'} + [C_2] + K_3'\,[\bar{S}]\,[C_2]$$

$$\text{or } [I_r(III)]_T = [C_2]\,\frac{[Cl^-]}{K_2'} + 1 + K_3'\,[S^-\,]$$

$$\text{or } [C_2] = \frac{K_2'\,[I_r(III)]_T}{[Cl^-] + K_2' + K_2'\,K_3'\,[\bar{S}\,]}$$

$$\text{or } [C_2] = \frac{K_2\,[I_r\,(III)]_T}{[Cl^-] + K_2'\,(1 + K_3'\,[S^-])} \qquad \dots (5)$$

By comparing eqns (1) and (5) we have

$$\frac{-d[Cu(II)^{*}]}{dt} = \frac{k_3 K_2^{'} [I_r(III)]_T [S^{-}]}{[Cl^{-}] + K_2^{'} (1 + K_3^{'} [S^{-}])} \qquad \ldots (6)$$

From step (1) we have

$$K_1 = \frac{[\bar{S}][H_2O]}{[S][OH^{-}]}$$

or $$[\bar{S}] = \frac{K_1}{[H_2O]} [S][OH^{-}] \qquad \ldots (7)$$

Now from eqns (6) and (7) we have eqn (8).

$$\frac{-d[Cu(II)^{*}]}{dt} = \frac{k_3 K_1^{'} K_2^{'} [I_r(III)]_T [S][OH^{-}]}{[Cl^{-}] + K_2^{'} \left(1 + \dfrac{K_1 K_3^{'} [S][OH^{-}]}{[H_2O]}\right)}$$

where $K_1^{'} = K_1/[H_2O]$ $\qquad \ldots (8)$

Further on assuming $$1 \gg \frac{K_1 K_3^{'} [S][OH^{-}]}{[H_2O]}$$

eqn (8) may be written as eqn (9)

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